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Spectrum of Barium Hydride — W. R. FREDRICKSON AND WILLIAM W. WATSON 753
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Fine Structure of the Visible Absorption Bands of Bromine — WELDON G. BROWN 777
Near Infrared Absorption Spectra of Some Halogen Derivatives of Methane — JOHN G. MOORHEAD 786
Absorption and Resonance of the Helium Infrared Lines — M. R. WEHR 796
Intensity Measurements in the Arc Spectrum of Thallium S. E. WILLIAMS AND J. HERLIHY 802
Intensities in Singlet-Triplet Bands of Diatomic Molecules — ROBERT SCHLAPP 806
Effect of Pressure upon the e.m.f. of the Weston Standard Cell — THOS. C. POULTER AND CARTER RITCHEY 816
Kinetic Interpretation of the Kelvin Relations — E. A. UEHLING 831
Hall Effect in Solid Mercury — JAMES T. SERDUKE AND THOMAS F. FISHER 831
On the Behavior of Non-Static Models of the Universe when the Cosmological Term is Omitted — RICHARD C. TOLMAN AND MORGAN WARD 835

Letters to the Editor

Diamagnetic Susceptibility of the Rare Gas Atoms According to Slater's Method W. ROSER ARNOLD 844
Shot Effect and Electrical Breakdown in Insulators — R. M. BOSWORTH AND F. E. HAWORTH 845
Isotopic Constitution of Zinc — KENNETH T. BAINBRIDGE 847

Book Reviews — 849

PROCEEDINGS OF THE AMERICAN PHYSICAL SOCIETY

New Orleans Meeting, December 29–30, 1931; Minutes and Abstracts, No. 1–64, Author Index 854
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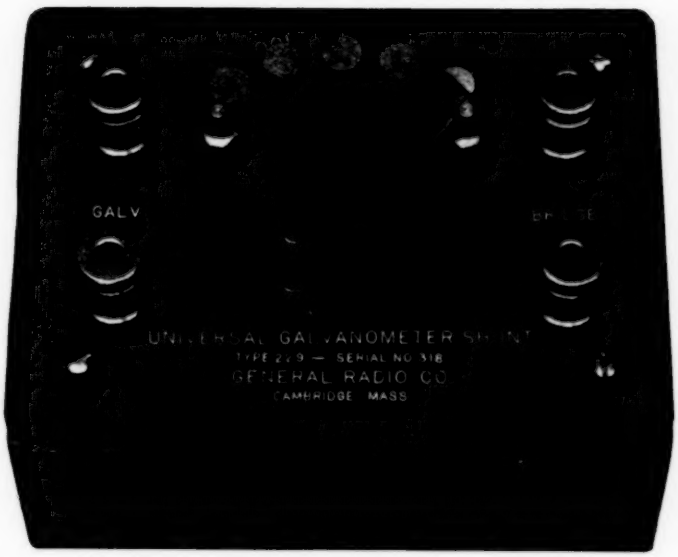

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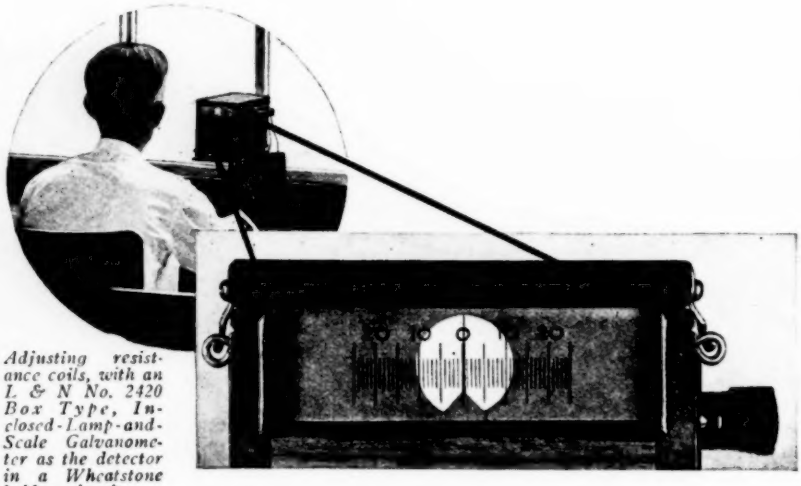

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PHYSICAL REVIEW

THE SPECTRUM OF BARIUM HYDRIDE

By W. R. Fredrickson, Syracuse University
and William W. Watson, Yale University

(Received January 8, 1932)

Abstract

A BaH band system in the region 6925A to 6380A has been photographed with a 21-foot grating (dispersion = 2.04A per mm), using a metallic barium arc in a hydrogen atmosphere at reduced pressure as a source. The spectrum consists of the (0, 0), (1, 1) and (2, 2) bands only, and the analysis of the (0, 0) band shows the system to be the expected $^2\Pi \rightarrow {}^2\Sigma$ case *a* type with twelve branches in each band. Assignments of the frequencies to these branches are presented, together with the principal combination differences. The Λ-type doubling is large in the $^2\Pi_{1/2}$ state, but small and of opposite sign in the $^2\Pi_{1\ 1/2}$ state, giving $p_0 = +0.85$ and $q_0 = +0.0067$. The spin doubling in the $^2\Sigma$ state is regular, with $\gamma_0 = +0.186$. Other constants are $B_0'' = 3.404$, $D_0'' = -9.61\times10^{-8}$, $r_0'' = 2.22\times10^{-8}$cm, $B_{0,-1/2}' = 3.4468$, $D_{0,-1/2}' = -1.13\times10^{-4}$, $B_{0,+1/2}' = 3.5156$, and $D_{0,+1/2}' = -1.20\times10^{-4}$. The separation of the two $^2\Pi$ sublevels yields $A = 462$. The smallness of this value ($A = 832$ for lowest ^3P levels of Ba) indicates that this state is possibly formed from a combination of the lowest ^3P and ^3D states of the Ba atom. A large perturbation in one of the $^2\Pi_{1\ 1/2d}$ levels, and the sign and magnitude of the p_0 and q_0, indicate another lower-lying excited level.

Introduction

THE band spectra which have so far been reported and analysed for diatomic hydrides of all the elements in the second column of the periodic table with the exception of Sr, Ba, and of course Ra involve transitions from excited $^2\Pi$ and $^2\Sigma$ states to a normal $^2\Sigma^+$ state [1] Among the $^2\Pi \rightarrow {}^2\Sigma$ bands are examples of all types of coupling in the $^2\Pi$ states from almost strictly case *b* for BeH ($A = 1.97$, $B = 10.3$), with thus only three branches in each band except for a barely resolvable doubling in each branch at the origin, to complete case *a* for HgH ($A = 3683$, $B = 6.58$) with a resulting twelve-branch structure for the bands. For the occurrence of twelve strong branches it is necessary for the doubling of the levels in the $^2\Sigma$ state to be appreciable in order that the satellite $^PQ_{12}$, $^QR_{12}$, $^QP_{21}$ and $^RQ_{21}$ branch lines be separated from the main-branch lines. The known $^2\Sigma$, $^2\Sigma$ bands for these molecules also display many variations attributable to resonance and perturbing effects on the upper states by other near-lying electronic levels.

[1] The references for the data for these bands, together with discussion of their characteristics, are given by R. S. Mulliken, Phys. Rev. **32**, 388 (1928); **33**, 507 (1929), and R. S. Mulliken and A. Christy, Phys. Rev. **38**, 87 (1931).

It was to be expected then that any $^2\Pi \rightarrow {}^2\Sigma$ band systems from the molecules SrH and BaH should contain twelve branches in each band and with fairly large spacing between the $^2\Pi_{1/2}$ and $^2\Pi_{1\,1/2}$ origins, since the constant A for the coupling between Λ and S could be expected to be almost as large as that for the ^3P states of Sr and Ba respectively. Furthermore, judging from the position of the corresponding bands for the other like molecules, it could be predicted that these bands should be found in the red region of the spectrum, near the lowest $^3P - {}^3S$ atomic lines. And since the electronic configurations of Ca, Sr, and Ba in the lowest levels are so similar, it was thought that a $^2\Sigma$, $^2\Sigma$ transition should lie very near to the $^2\Pi \rightarrow {}^2\Sigma$ for SrH and BaH as in the case of CaH, but possibly exhibiting still larger doublings due to the l-uncoupling phenomenon. Precisely this situation has been found to exist in the spectrum of SrH which is described in detail in the following paper. The present paper discusses the spectrum of BaH, which consists principally only of the $^2\Pi \rightarrow {}^2\Sigma$ system, but with strong indications of another band system too far into the red to be photographed.

Experimental Procedure

As a source a 110-volt d.c. arc carrying 3 amperes between an anode made of a small piece of metallic barium and a thin flat piece of copper as the cathode was used. This arc was operated in the modified Back chamber mounted between the poles of a large Weiss electromagnet which happened to be in position in front of the slit of the spectrograph. The barium electrodes were about $6 \times 6 \times 4$ mm in size carried at the end of a short length of tungsten wire. Hydrogen at about 5 cm pressure was pumped slowly through the arc chamber during the exposure. It was found that the molecular spectrum was emitted much more strongly from a continuous arc than from the intermittent form of arc employed in the Zeeman effect work. The consumption of four of these small pieces of Ba in the arc sufficed to give intense spectrograms of the BaH bands at the red end in the dicyanine region.

The spectrograms were obtained in the second order of a 21-foot concave grating in a stigmatic mounting, the dispersion being about 2.04A per mm. A very strong band system, which the analysis given below shows to be a $^2\Pi \rightarrow {}^2\Sigma$ transition for BaH, in the near red between 6380A and 6925A is emitted by this source. Eastman panchromatic plates dyed with dicyanine to give greater sensitivity at the long wave-length end were used. Fig. 1 is a reproduction of this band system. In addition to these bands, this arc emits a molecular spectrum in the green and yellow regions of the visible spectrum consisting of a considerable density of lines with but little evidence of regularity. This sytem is perhaps analogous to a $^2\Sigma$, $^2\Sigma$ band system for CaH recently partly analysed by Grundström,[2] and will be investigated later. There is also strong evidence for the existence of another band system still farther into the near infrared, but a spectrogram in the first order taken with a neocyanine-dyed plate fails to reveal it.

[2] B. Grundstrom, Zeits. f. Physik **33**, 235 (1931).

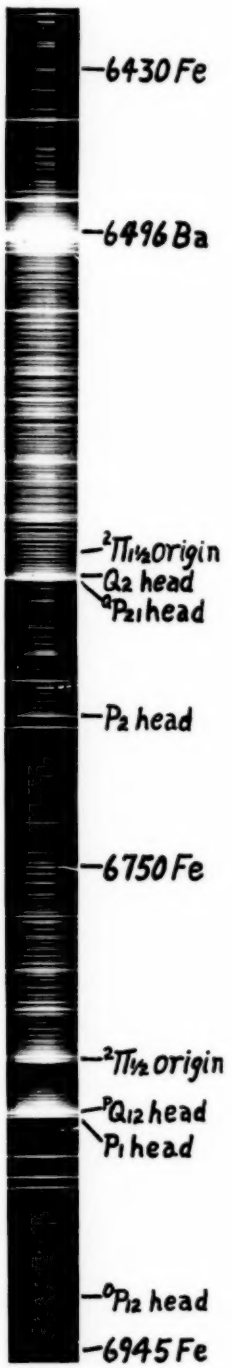

Fig. 1. Reproduction of the $^2\Pi$, $^2\Sigma$ BaH band lying between 6380A and 6925A. Note the considerable spacing between the heads of the satellite and main branches, and their equal intensity.

Details of the $^2\Pi \rightarrow {}^2\Sigma$ Band

The (0,0), (1,1), and (2,2) bands are present in this sytem, and analysis of the (0,0) bands reveals twelve branches in a band. In Fig. 1 the double-headed appearance of the band due to the turning of the P_1 and $^PQ_{12}$ branches can be seen. Since it is known that the separation of these branches is due to the doubling of the levels of the $^2\Sigma$ state and that the separation of the lines having the same K values should be proportional to $K+\frac{1}{2}$, it was at once possible to assign J values to the lines of these series. A similar procedure was employed in determining the Q_1 and $^QR_{12}$, $^QP_{21}$ and Q_2, and $^RQ_{21}$ and R_2 branches. The other series were found by applying various internal combinations which can be determined from an energy level diagram for a $^2\Pi \rightarrow {}^2\Sigma$ transition.[3,4] All series are regular with the exception of a perturbation in the

Table I. *Assignment of lines for the (0, 0) band of* $^2\Pi \rightarrow {}^2\Sigma$ *system of BaH* (cm^{-1} units; *b* indicates a broad line due to the fusion of two or more lines; *A* an atomic line).

			$^2\Pi_{1/2} \rightarrow {}^2\Sigma$			
$J''+\frac{1}{2}$	$^0P_{12}$	P_1	$^PQ_{12}$	Q_1	$^QR_{12}$	R_1
1			14625.82	14633.17	14637.76	14642.83
2		14625.43	22.36	37.24	41.98	52.30
3		21.90	19.21	41.29	46.35	62.39
4		18.50	16.20	45.74	51.01	72.76
5	14586.35	15.32	13.42	50.25	55.81	83.33
6	77.83	12.47	10.79	54.98	60.78	694.06
7	69.69	09.68	08.60	59.89	66.54	705.09
8	61.30	07.04	06.34	65.10	72.09	16.20
9	53.40	04.46	04.46	70.41	77.80	27.52
10	45.77	02.70	02.70	76.01	83.67	38.89
11	38.35	14600.77	01.32	81.63	89.76	50.65
12	31.12	14599.16	14600.13	87.46	14695.95	62.45
13	24.22	97.80	14599.23	93.58	14702.41	74.40
14	17.49	96.63	98.35	14699.79	08.78	86.44
15	11.09	95.63	97.88	14706.24	15.76	14798.88
16	14504.83	94.92	97.58	12.77	22.57	14811.31
17	14498.86	94.50	97.20	19.58	29.57	23.94
18	93.16	94.00	97.52	26.43	37.11	36.74
19	87.73	94.21	98.04	33.59	44.59	49.70
20	82.58	94.42	98.70	40.89	52.23	62.83
21	77.77	94.92	99.61	48.37	59.99b	76.09
22	73.15	95.63	00.86	55.97	67.96b	14889.39
23	68.79	96.63	02.19	63.74	76.02	14902.87
24	64.74	97.80	03.80	71.72	84.41	16.42
25	60.97	14599.16	05.64	79.86	14792.69	30.29
26	57.46	14600.86	07.55	87.98	14801.57	44.50
27	54.09	02.70	09.68	14796.67	10.48	58.23
28	51.42	04.46	12.47	14805.29	19.30	72.12
29	48.81	07.09	15.30	14.15	28.68	14986.49
30	46.51	09.68	18.44	23.07	37.62	15000.67
31	44.42	13.42		32.13	46.85b	
32	42.71	16.20		41.25	55.85	
33	41.26	19.21		50.49		
34	39.93					

[3] The energy diagram for HgH given by R. S. Mulliken (Reviews of Modern Physics **3**, 130 (1931)) could well represent the facts for BaH by choosing a suitable scale.

[4] One of the internal combinations used is:

$$Q_1(J) - {}^0P_{12}(J+1) = R_1(J) - {}^PQ_{12}(J+1) = {}^SR_{21}(J) - Q_2(J+1)$$
$$= {}^RQ_{21}(J) - P_2(J+1) = F_2''(J+1) - F_1''(J).$$

This one combination involves eight of the twelve branches.

TABLE I. (*Continued*).

			$^2\Pi_{1\,1/2} \rightarrow {}^2\Sigma$			
$J''+\frac{1}{2}$	P_2	$^QP_{21}$	Q_2	$^RQ_{21}$	R_2	$^SR_{21}$
1					15092.20	15098.69
2			15078.32	15091.50	96.19	15109.90
3		15077.72	75.94	95.51	15100.65	20.44
4	15048.96	75.94	73.94	99.95	05.47b	31.74
5	40.59	73.38	72.26	15104.75	10.94b	43.41
6	32.29	71.38	70.92	09.90	16.39	55.64
7	24.26	69.76	70.35b	15.51b	22.54	67.98
8	16.63	68.62	69.39	21.19	28.77	80.69
9	09.53	67.85	68.99	27.14	35.51	15193.76
10	15002.53	67.39	69.12	33.50	42.38	15207.11
11	14996.06	67.01	69.45	40.42	52.17	20.67
12	89.80	67.38	70.16	50.43b	58.00b	34.55
13	86.79	67.85	71.29	55.41	65.53	48.77
14	79.21	68.73	72.82	61.97	73.71	63.29
15	74.22	70.00	74.59	71.03	82.22	78.03
16	69.59	71.38	76.67	79.36	15191.17	15293.01
17	65.46	73.94	79.15	87.95	15200.26	15308.23
18	61.63	75.84	81.90	15196.94	09.53	23.68
19	58.23	78.50	84.98	15206.17	19.34	39.42
20	55.26	81.40	88.42	15.79	29.37	55.43b
21	52.37	84.68	92.20	25.55	39.63	71.49
22	50.15	88.42	15096.19	35.54	50.11	15388.00A
23	48.32	92.20	15100.65	45.94	60.88	15404.46
24	46.89	15096.19	05.43	56.59	71.91	20.90A
25	45.75	15100.65	10.39	67.41	83.21	38.13
26	44.95	05.45b	15.51	78.68	15294.71	55.19
27	44.47	10.94b	21.19	15289.82	15306.48	72.40
28	44.47	16.29	27.14	15301.41	18.27	15489.72
29	44.95	22.07	33.34	13.27	30.65	15507.30
30	45.75	27.52	39.86	25.09	43.01	25.10
31	46.89		46.68	37.56	55.43	42.92
32	48.32		53.64	49.97	68.51	61.02
33	50.15		61.03	62.65	81.34	
34	52.37		68.56	75.55	15394.75	
35	55.26		76.31	15388.77	15408.04	
36			84.53	15401.84	21.62	
37			93.15	15.22	35.23	
38				28.82	49.37	
39				56.31	63.08	
40				70.31	77.19	
41				84.29	91.38	

P_2, R_2, and $^RQ_{12}$ branches due to a perturbation of the $^2\Pi_{1\,1/2d}$ levels around $J'=11\frac{1}{2}$. The frequencies of the lines of the twelve branches of the (0,0) band are listed in Table I.

In addition to forming a test of the correctness of the assignments of the band lines to the several branches, the combination differences also serve in the calculation of the molecular constants. The following combinations involving the terms of the lower state may be verified with the aid of the energy level diagram:

$$R_1(J-1) - P_1(J+1) = {}^SR_{21}(J-1) - {}^QP_{21}(J+1)$$
$$= F_1''(J+1) - F_1''(J-1) = \Delta_2F_1''(J)$$

and

$$R_2(J-1) - P_2(J+1) = {}^QR_{12}(J-1) - {}^OP_{12}(J+1) \qquad (1)$$
$$= F_2''(J+1) - F_2''(J-1) = \Delta_2F_2''(J).$$

These combinations for this BaH band are listed in Table II. The $\Delta_2F_1''(J)$ values are slightly larger than the $\Delta_2F_2''(J)$ due to the spin doubling in the $^2\Sigma$ state. The last column of the table gives the average of the four combination values, and is the one from which the constants are calculated (cf. next section).

TABLE II. *Lower state combinations.* The 1st set of data gives the $\Delta_2F_1''(J)$ values obtained from Eq. (1); the second set, the $\Delta_2F_2''(J)$. The J values have been omitted in headings; $R_1-P_1=R_1(J-1)-P_1(J+1)$, etc. The $\Delta_2F''(K)$ values in the last column are the average of $\Delta_2F_1''(J=K+\frac{1}{2})$ and $\Delta_2F_2''(J=K-\frac{1}{2})$, used in Eq. (3).

	$\Delta_2F_1''(J)$				$\Delta_2F_2''(J)$					
$J''+\frac{1}{2}$	R_1-P_1	${}^SR_{21}-{}^QP_{21}$	Av.	$J''+\frac{1}{2}$	R_2-P_2	${}^QR_{12}-{}^OP_{12}$	Av.	K	$\Delta_2F''(K)$
2	20.93	20.97	20.95					1	20.95
3	33.80	33.96	33.88					2	33.88
4	47.07	47.06	47.06	4	60.06	60.00	60.03	3	47.06
5	60.29	60.36	60.33	5	73.18	73.18	73.18	4	60.18
6	73.65	73.65	73.65	6	86.68	86.12	86.40	5	73.42
7	87.02	87.00	87.01	7	99.76	99.48	99.62	6	86.70
8	100.63	100.63	100.63	8	113.01	113.14	113.07	7	100.12
9	113.50	113.30	113.40	9	126.24	126.32	126.28	8	113.23
10	126.75	126.75	126.75	10	139.45	139.45	139.45	9	126.51
11	139.73	139.73	139.73	11	152.58	152.55	152.57	10	139.59
12	152.85	152.85	152.85	12	165.38	165.53	165.45	11	152.71
13	165.82	165.82	165.82	13	178.03	178.46	178.25	12	165.63
14	178.77	178.77	178.77	14	191.31	191.32	191.31	13	178.51
15	191.52	191.91	191.71	15	204.12	203.95	204.03	14	191.51
16	204.38	204.09	204.23	16	216.76	216.90	216.83	15	204.13
17	217.31	217.17	217.24	17	229.54	229.41	229.48	16	217.03
18	229.44	229.73	229.58	18	242.03	241.84	241.93	17	229.53
19	242.57	242.28	242.42	19	254.27	254.53	254.40	18	242.17
20	254.86	254.74	254.80	20	266.97	266.82	266.90	19	254.60
21	267.20	267.01	267.11	21	279.22	279.08	279.15	20	267.00
22	279.46	279.29	279.37	22	291.31	291.20	291.25	21	279.26
23	291.59	291.81	291.70	23	303.22	303.22	303.22	22	291.47
24	303.71	303.81	303.76	24	315.13	315.05	315.09	23	303.49
25	315.56	315.45	315.50	25	326.95	326.96	326.95	24	315.29
26	327.59	327.19	327.19	26	338.74	338.60	338.67	25	327.07
27	340.04	338.90	338.90	27	350.14	350.15	350.15	26	338.79
28	351.14	350.33	350.74	28	361.53	361.53	361.53	27	350.44
29	362.44	362.33	362.38	29	372.52	372.71	372.61	28	361.95
30	373.07	372.85	372.96	30	383.76	383.76	383.76	29	372.78
				31	394.69	394.91	394.80		
				32	405.28	405.59	405.44		
				33	416.14	415.92	416.03		

The combinations involving the upper state are the following:

$$\begin{aligned} R_1(J) - P_1(J) &= F_{1d}'(J+1) - F_{1d}'(J-1) = \Delta_2F_{1d}'(J) \\ {}^QR_{12}(J) - {}^OP_{12}(J) &= F_{1c}'(J+1) - F_{1c}'(J-1) = \Delta_2F_{1c}'(J) \\ R_2(J) - P_2(J) &= F_{2d}'(J+1) - F_{2d}'(J-1) = \Delta_2F_{2d}'(J) \\ {}^SR_{21}(J) - {}^QP_{21}(J) &= F_{2c}'(J+1) - F_{2c}'(J-1) = \Delta_2F_{2c}'(J). \end{aligned} \tag{2}$$

These upper state combinations are tabulated in Table III. Large differences exist between the $\Delta_2F_{1d}'(J)$ and $\Delta_2F_{1c}'(J)$ values due to the large Λ-type doubling in the $\Pi_{1/2}$ state, while but small differences are noted between $\Delta_2F_{2d}'(J)$ and $\Delta_2F_{2c}'(J)$, corresponding to a small Λ-type doubling in the $\Pi_{1\,1/2}$ state. However, for purposes of calculation of constants the average of each group (designated Δ_2F_{dc}') is taken.

TABLE III. *Upper state combinations.* The Δ_2F' headings are defined by Equations (2). $\Delta_2F_{1dc}'(J)$ is the average of $\Delta_2F_{1c}(J)$ and $\Delta_2F_{1d}(J)$. Likewise, $\Delta_2F_{2dc}'(J)$ is average of $\Delta_2F_{2d}'(J)$ and $\Delta_2F_{2c}'(J)$. The values marked p involve perturbed levels, and are therefore not included in the averages.

$J''+\frac{1}{2}$	$\Delta_2F_{1d}'(J)$	$\Delta_2F_{1c}'(J)$	$\Delta_2F_{1dc}'(J)$	$J''+\frac{1}{2}$	$\Delta_2F_{2d}'(J)$	$\Delta_2F_{2c}'(J)$	$\Delta_2F_{2dc}'(J)$
2	26.87						
3	40.49			3		42.72	
4	54.26			4	56.51	55.80	56.16
5	68.01	69.46	68.73	5	70.35	70.03	70.19
6	81.59	82.95	82.27	6	84.10	84.26	84.18
7	95.41	96.85	96.13	7	98.28	98.22	98.25
8	109.16	110.79	109.98	8	112.14	112.07	112.10
9	123.06	124.40	123.73	9	125.94	125.91	125.95
10	136.19	137.90	137.05	10	139.85	139.72	139.78
11	149.88	151.41	150.65	11	156.14p	153.66	153.66
12	163.29	164.83	164.06	12	168.20p	167.17	167.17
13	176.60	178.19	177.39	13	178.84p	180.92	180.92
14	189.81	191.29	190.55	14	194.50	194.56	194.53
15	203.25	204.67	203.96	15	208.00	208.03	208.01
16	216.39	217.74	217.07	16	221.58	221.63	221.61
17	229.44	230.71	230.13	17	234.80	234.29	234.54
18	242.74	243.95	243.45	18	247.90	247.84	247.87
19	255.49	256.86	256.17	19	261.11	260.92	261.01
20	268.41	269.65	269.03	20	274.11	274.03	274.07
21	281.17	282.22	281.70	21	287.26	286.81	286.54
22	293.76	294.81	294.28	22	299.99	299.58	299.78
23	306.24	307.23	306.74	23	312.56	312.26	312.41
24	318.62	319.67	319.15	24	325.02	324.71	324.87
25	331.13	331.72	331.43	25	337.56	337.48	337.52
26	343.64	344.11	343.87	26	349.76	349.74	349.75
27	355.53	356.39	355.96	27	362.00	361.46	361.74
28	367.66	367.88	367.77	28	373.80	373.43	373.61
29	379.40	379.87	379.63	29	385.90	385.23	385.57
30	390.99	391.11	391.05	30	397.27	397.58	397.42
31		402.43		31	408.54		408.54
				32	420.19		420.19
				33	431.19		431.19
				34	442.38		442.38
				35	452.78		452.78

EVALUATION OF CONSTANTS B, D, AND A

The energy equation[5] for the terms of the normal $^2\Sigma$ state, which is typical case b, is

$$T(J) = T_0^e + T^v + B''[K(K+1) + G^2] + \gamma''[J(J+1) - K(K+1) - S(S+1)] + D''K^2(K+1)^2$$

with $S=\frac{1}{2}$.

Representing by $T_1(K)$ the states with $J=K+S$ and by $T_2(K)$ the states with $J=K-S$, it is easily seen that $T(K)=\frac{1}{2}\{T_1(K)+T_2(K)\}$ is given by the equation

$$T''(K) = T_0^e + T^v + B''[K(K+1) - G^2] + D''K^2(K+1)^2 + S\gamma$$

from which one obtains

$$\Delta_2F''(K) = B''(4K+2) + D''(8K^3 + 12K^2 + 12K + 4). \qquad (3)$$

The application of this equation to the experimental values given in the last column of Table II yields the B'' and D'' given in Table IV.

[5] R. S. Mulliken, Rev. Mod. Phys. **2**, 106–107 (1930).

TABLE IV. *Constants resulting from the analysis of the* $^2\Pi \rightarrow {}^2\Sigma$ *(0, 0) band of BaH* (cm^{-1} *units*).

$B_0'' = 3.404$	$D_0'' = -9.61 \times 10^{-5}$
$B_{0,-1/2}' = 3.4468$	$D_{0,-1/2}' = -1.13 \times 10^{-4}$
$B_{0,+1/2}' = 3.5156$	$D_{0,+1/2}' = -1.20 \times 10^{-4}$

$^2\Sigma$ state: $\gamma_0 = +0.186$, $r_0'' = 2.22 \times 10^{-8}$ cm
$^2\Pi$ state: $p_0 = +0.85$, $q_0 = +0.0067$, $A = 462$.

The term values for the $^2\Pi$ state may be represented by an equation which Mulliken and Christy[6] have adopted from Van Vleck's[7] theoretical paper on Λ-type doubling. This equation takes into account the effects of spin and Λ-type doubling, and if $|A| \ll |\nu(\Pi, \Sigma)|$ may be written

$$\begin{aligned} T(J) = {} & T_0 + B_v\{(J+\tfrac{1}{2})^2 - 1 \pm \tfrac{1}{2}X\} + \tfrac{1}{2}\{o + \tfrac{1}{2}p^* + q^*(J+\tfrac{1}{2})^2\} \\ & \pm \tfrac{1}{2}X^{-1}\{(2-Y)(o+\tfrac{1}{2}p^*+q^*) + (p^*+2q^*)(J-\tfrac{1}{2})(J+1\tfrac{1}{2})\} \\ & + [\pm]\tfrac{1}{2}(J+\tfrac{1}{2})\{[\pm 1 + X^{-1}(2-Y)](\tfrac{1}{2}p+q) + 2X^{-1}q(J-\tfrac{1}{2})(J+1\tfrac{1}{2})\} \\ & + D(J+\tfrac{1}{2})^4. \end{aligned}$$

For the meaning of all terms reference should be made to Mulliken and Christy's paper. As to the signs, whenever the sign $\pm$ occurs the upper sign refers to T_2 states and the lower sign to T_1 states, while whenever the bracketed sign $[\pm]$ occurs the $+$ sign refers to T_d levels and the $-$ sign to T_c levels.

If we take the average of $T_d(J)$ and $T_c(J)$ the third line in the above equation disappears, since one would involve the $+$ sign and the other the $-$ sign. Hence, the average energy term $T_{dc}(J) = \frac{1}{2}\{T_d(J) + T_c(J)\}$ becomes

$$T_{dc}(J) = T_0 + J(J+1)\left[B_v \pm \frac{B_v^2}{A} + \frac{q^*}{2} \pm \frac{p+2q}{2X}\right] + D[J^2(J^2+1)]$$

$+$(terms independent of J or the J involved in X terms).

Setting

$$B_\Sigma^* = \left[B_v + \frac{q^*}{2} \pm \left(\frac{B_v^2}{A^2} + \frac{p+2q}{2X}\right)\right]$$

with $\pm$ sign according as $\Sigma = \pm\frac{1}{2}$, one obtains the customary form of $\Delta_2 F$ equation:

$$\Delta_2 F_{dc}(J) = B_\Sigma^*(4J+2) + D_\Sigma'(8J^3 + 12J^2 + 12J + 4). \qquad (4)$$

Applying this equation to the average $\Delta_2 F_{dc}(J)$'s given in Table III, the B' and D' values given in Table IV were obtained.[8]

The coupling constant A is determined in the usual way from the Hill and Van Vleck equation

$$T_0 = T_0^e + G(v) + B_v\{(J+\tfrac{1}{2})^2 - \Lambda^2 \pm \tfrac{1}{2}[4(J+\tfrac{1}{2})^2 - 4A^2\Lambda^2/B + A^2\Lambda^2/B_v^2]\}.$$

By taking the difference of two band frequencies, one near each origin, which have the same lower state but arise from different upper states, one of

[6] R. S. Mulliken and A. Christy, Phys. Rev. **38**, 87 (1931).

[7] J. H. Van Vleck, Phys. Rev. **33**, 406 (1929).

[8] Computation of $B_{0,-1/2}$ with the $\Delta_2 F_{1c}(J)$ and $\Delta_2 F_{1d}(J)$ values of Table III separately gives 3.4762 and 3.4175 respectively. The $B_{0,-1/2} = 3.4468$ given in Table IV is the mean of these two values.

which is a T_1 state and the other a T_2 state, a quadratic equation in A and B is obtained. By selecting, then, another suitable pair of frequencies a second equation is evaluated, and A can be found by solving the two equations simultaneously. The average of a number of such determinations has led to the value $A=462$ as given in Table IV.[9] This value of A is much smaller than the A expected from the value 832 of the corresponding L, S coupling of the lowest ^3P state of Ba (*cf.* discussion below).

Spin and Λ-Type Doubling

It is of interest to investigate the spin and Λ-type doubling in bands because of the light thus thrown on the probable electron configurations of the molecular states involved. The theoretical work of Van Vleck[7] has been interpreted in a detailed paper by Mulliken and Christy[6] with applications to many known band systems. The spin doubling is defined by $\Delta\nu_{12}(K)=T_1(K)-T_2(K)$;—the separation of T_1 and T_2 levels having the same K value. Theoretically,

$$\Delta\nu_{12}(K)=\gamma(K+\tfrac{1}{2}) \tag{5}$$

experimentally it is determined from the separation of the corresponding lines in P_1 and $^PQ_{12}$, Q_1 and $^QR_{12}$, $^QP_{21}$ and Q_2, and $^RQ_{12}$ and R_2 branches with the same K.

The Λ-type doubling is defined as $\Delta\nu_{dc}(J)=T_d(J)-T_c(J)$;—the separation of T_d and T_c levels with the same J. Theoretically, for case $a\Delta\nu_{dc}(J)=-p(J+\frac{1}{2})$ for a $^2\Pi_{1/2}$ state and

$$\Delta\nu_{dc}(J)=\left(\frac{p}{Y^2}+\frac{2q}{Y}\right)(J-\tfrac{1}{2})(J+\tfrac{1}{2})(J+1\tfrac{1}{2})$$

for a $^2\Pi_{11/2}$ state; experimentally, the Λ-type doubling is obtained from the relation

$$\Delta\nu_{dc}(J+\tfrac{1}{2})=\tfrac{1}{2}\{[R(J)-Q(J)]-[Q(J+1)-P(J+1)]\}. \tag{7}$$

Figure 2 shows the spin and Λ-type doubling for these BaH states. Each point on the spin doubling curve is the average of the four values obtained. The curve varies linearly with $(K+\frac{1}{2})$ as expected, the slope giving the value of γ listed in Table IV. The Λ-type doubling in the $^2\Pi_{1/2}$ state is large and negative, while in the $^2\Pi_{1\,1/2}$ state it is small and positive. It is interesting to note that the doubling in the $^2\Pi_{1\,1/2}$ state is practically zero until the perturbed level is reached, from which point it appears to increase as shown. The values of p and q calculated from equations (6) are given in Table IV.

[9] Theoretically, A could be determined from the values of $B_\Sigma{}^*$. For instance, the value X could be assumed to have value Y for low J's since the value of Y is large ($Y=A/B=125$). Thus $B_\Sigma{}^*=B_v+q\pm 1/A\,[B_v{}^2+B_v{}^*(p+2q/2)]$ where p and q have the values given in Table IV. Actual calculation by this method gives $A=395$, which is much lower than the best value 462. The disagreement is due to (1) approximations made in obtaining B_Σ and (2) slight errors in $B_\Sigma{}^*$ causing a large error in constants (for example, a difference of 0.01 in B^* causes a difference of 70 in A).

The effect of Λ-type doubling on the relative position of the four levels of the $^2\Pi$ state as K' increases is shown in Fig. 3. All term values are calculated with $T_{1d}(J)$ assumed equal to zero; the separation of T_{1c} and T_{1d} levels is obtained directly from $\Delta\nu_{dc}(J)$ values for the $^2\Pi_{1/2}$ state; T_{2d} is computed from the difference in wave number of the lines $P_2(J) - {}^PQ_{12}(J) = T_{2d}(K') - T_{1d}(K')$ where $K' = J'' + \frac{1}{2}$; and finally, T_{2c} values are obtained from $T_{2d} + \Delta\nu_{dc}(J)$ for the $^2\Pi_{1\,1/2}$ state, using however the interpolated values of $\Delta\nu_{dc}(J)$ for the actual K' level.

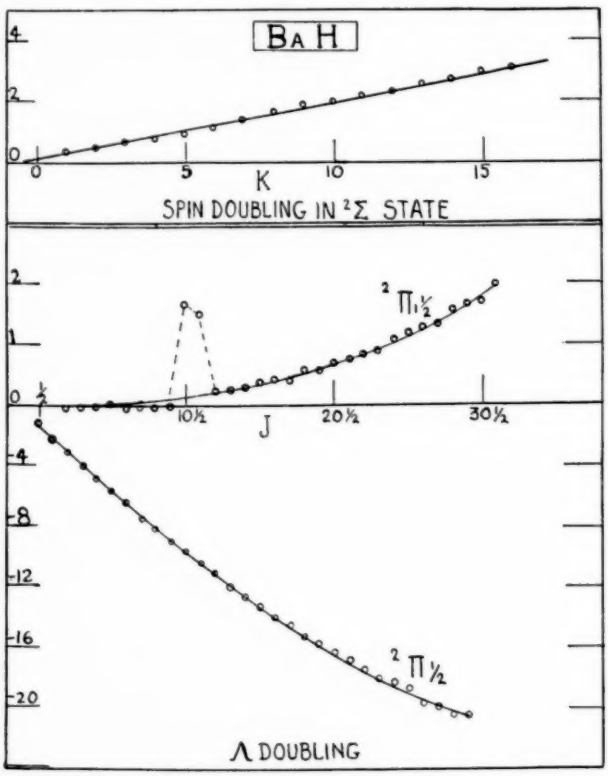

Fig. 2. Spin doubling in the normal $^2\Sigma$ state and Λ-type doubling in the $^2\Pi$ state of BaH. The linear doubling relation for the $^2\Sigma$ state is apparent. Note that the Λ-type doubling is large in the $^2\Pi_{1/2}$ levels, while it is small and of opposite sign in the $^2\Pi_{1\,1/2}$ levels. The irregularity in the $^2\Pi_{1\,1/2}$ curve is due to the perturbation caused by some lower-lying excited level of BaH.

Comparison of Fig. 3 with similar graphs for SrH (Fig. 3 in following paper) and CaH[10] brings out certain interesting features. In BaH the T_{1c} levels are above the T_{1d} levels while the T_{2c} levels are below the T_{2d}. The opposite is true for SrH and for low K values for CaH. The doubling in the $^2\Pi_{1\,1/2}$ state is very small indeed, as predicted for case *a* by Van Vleck's theory, while the increase of doubling in the corresponding state of SrH and CaH shows that each in turn approaches closer to case *b* with increase in the molecular rotation. Also, the $^2\Pi_{1/2}$ level separations should be large for case *a* but

[10] Reference 6, p. 117.

should decrease and finally change sign as case b is approached. It is observed that in BaH these levels do not begin this tendency toward case b—even at the highest K we have observed, while the SrH level does start bending back at $K'=28$, and for CaH it starts back at $K'=6$, passing through zero at $K'=11$.

Mulliken and Christy[6] have shown that Van Vleck's case of "pure precession", or something closely akin to it, exists between some of the known states of most diatomic molecules. In this case at least one electron has a well-defined l shared between say a Π state with $\lambda=1$ and a Σ state with $\lambda=0$. Then the γ, p, q constants have the following values

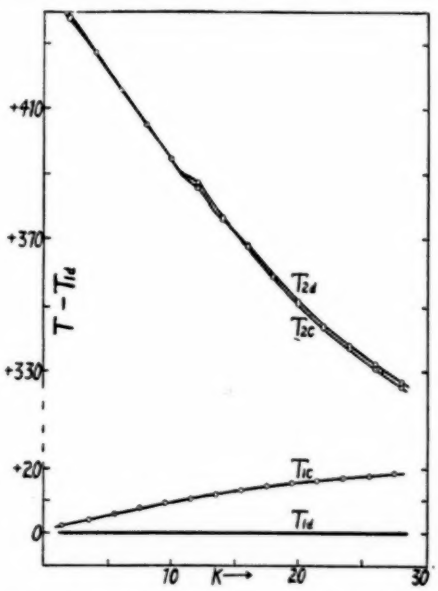

Fig. 3. Relative position of levels in the $^2\Pi$ state of BaH. The doublet interval $T_{2d}-T_2$ is very small, since the coupling is strictly case a. And for the same reason there is no tendency observable up to $J=30\frac{1}{2}$ for the T_1 levels to begin to come together.

$$\gamma = p = 2AB_v\, l(l+1)/\nu(\Pi,\Sigma)$$

and (8)

$$q = 2B_v^2\, l(l+1)/\nu(\Pi,\Sigma)$$

where A, B, and l have their usual meaning, and $\nu(\Pi,\Sigma)$ is the wave number difference of the Π and Σ states which have the common l. This $\nu(\Pi,\Sigma)$ is positive or negative as Π is higher or lower than Σ.

The disagreement between the observed γ and p values for the normal $^2\Sigma$ and this $^2\Pi$ state of BaH leads to the conclusion that the case of pure precession does not exist between these two states. Hence, since these states do not have a common l they must arise from different electronic configurations. But from the sign and magnitude of p and q and the calculated values of A and B, computation with Eq. (8) with $l=1$ leads to the conclusion that a

case of pure precession does exist between the known $^2\Pi$ state and an unknown excited $^2\Sigma^+$ state some 7000 wave numbers below the $^2\Pi$ state. Unfortunately a band system arising from a transition from this predicted $^2\Sigma$ state to the normal $^2\Sigma$ state of BaH would lie too far into the infrared to be photographed. This may be the state a level of which is causing the perturbation observed at $J=11\frac{1}{2}$ in the $^2\Pi_{1\ 1/2}$ state.

Discussion

The probable electron configuration of the BaH molecule in these states is not as readily determined as for the other similar hydride molecules. As Mulliken and Christy have pointed out, the fact that for CaH the observed p_0 and q_0 constants of the $^2\Pi$ state and the γ_0 for the doubling in the upper $^2\Sigma$ state indicate clearly that these two states have a relation of pure precession between them with $l=1$ makes it very probable that these two states of CaH are $\cdots 4p\pi$ and $\cdots 4p\sigma$. The normal $^2\Sigma$ state of CaH may then possibly be $\cdots 3d\sigma$, since in the Ca atom the $3d$ electron is almost as firmly bound as the $4p$. In SrH, as is shown in the following paper, an almost identical arrangement of levels is found. For BaH also, as has been demonstrated, there exists no pure precession relation between the $^2\Pi$ and the normal $^2\Sigma$ states. But there is the evidence cited that interaction does occur between the $^2\Pi$ state and an excited $^2\Sigma^+$ state below it. The fact that this $^2\Sigma$ state lies below the $^2\Pi$ is just what one would normally expect if they are really $\cdots 6p\sigma$ and $\cdots 6p\pi$ respectively.

This $^2\Pi$ BaH state is unique among the corresponding $^2\Pi$ states of these hydrides of the elements in the second column of the periodic table, however, in having its coupling constant A for the S, Λ interaction differing very considerably from the A for the lowest ^3P level of the atom concerned. Now Ba is the only one of these atoms for which the lowest ^3D level is *below* the lowest ^3P level, the interval being 0.41 volt. It may be that in the formation of the BaH molecule, these two atomic levels are forced together and combine to form the molecular $^2\Pi$ state with this lowered A constant. The dissociation relations would then be quite complicated. It is unfortunate that the indicated bands farther into the red cannot be investigated in order to note the interaction existing between their upper state and this "hybrid" $^2\Pi$ state.

We wish to thank Dr. Alden J. King for the supply of pure barium presented to us for this research, and we are indebted to Professor R. S. Mulliken for helpful discussion on the subject of electron configurations.

THE SPECTRUM OF STRONTIUM HYDRIDE

By William W. Watson, Yale University
and W. R. Fredrickson, Syracuse University

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Abstract

With a metallic strontium arc in a hydrogen atmosphere as a source, high dispersion spectrograms of three groups of bands in the near infrared with main heads at 7020A, 7347A and 7508A have been obtained. Analysis shows that the latter two groups of bands constitute a $^2\Pi \rightarrow {}^2\Sigma$ system with only the (0, 0) and (1, 1) vibrational transitions, while the first group represents a transition from a higher $^2\Sigma$ to the same normal $^2\Sigma$ state. Quantum analyses of the (0, 0) bands give for the normal $^2\Sigma$ state $B_0'' = 3.6198$ and $D_0'' = -1.287 \times 10^{-4}$, $r_0 = 2.16 \times 10^{-8}$ cm. For the $^2\Pi$ state, $A = 299$, $B_{0,-1/2}' = 3.6683$, $D_{0,-1/2}' = -1.33 \times 10^{-4}$, $B_{0,+1/2}' = 3.6787$ and $D_{0,+1/2}' = 1.13 \times 10^{-4}$. The rotational energy constants for the upper $^2\Sigma$ state are $B_0' = 3.8318$ and $D_0' = -1.641 \times 10^{-4}$. The spin doubling constant γ_0 in the normal state is $+0.122$, in the upper $^2\Sigma$ state it is -3.81, while from the Λ-type doubling in the $^2\Pi$ state $p_0 = -3.92$ and $q_0 = -0.398$. The doubling in the $^2\Sigma$, $^2\Sigma$ band is much the largest yet found in bands of this type. From the near equality of the p_0 of the $^2\Pi$ and the γ_0 of the upper $^2\Sigma$ and their close agreement with calculated values, it is to be concluded that these two states stand to each other in the relation of "pure precession", as is the case for the corresponding states of CaH. The probable electron configurations are then $\cdots 5p\pi$ and $\cdots 5p\sigma$ for the $^2\Pi$ and upper $^2\Sigma$ states and $\cdots 4d\sigma$ for the normal state.

Introduction

Because of the great similarity in the character and relative positions of the lowest levels of the Sr and Ca atoms, one would expect that the band spectra of the SrH and CaH molecules should be somewhat alike. The $^2\Pi \rightarrow {}^2\Sigma$ and $^2\Sigma \rightarrow {}^2\Sigma$ band systems of the CaH molecule show several interesting features because of the large interaction between the $^2\Pi$ and the upper $^2\Sigma$ states.[1] These two states lie but 1320 cm^{-1} apart, and from the magnitude of the observed doublings the amount of l-uncoupling is calculated to be very considerable, the component ρ of l along the direction of the rotational quantum number K being about 0.25 ($l = 1$) when $K = 33$. In view of the "pure precession" relation existing between these states, Mulliken and Christy conclude that the electron configurations are $\cdots 4\ p\pi$ and $\cdots 4\ p\sigma$ for the $^2\Pi$ and upper $^2\Sigma$ states respectively. This makes it possible that the normal $^2\Sigma$ state of CaH is $\cdots 3\ d\sigma$, since in the Ca atom the $3d$ electron is almost as firmly bound as the $4p$. In the Sr atom the $4d$ electron is also almost as firmly bound as the $5p$, with the energy difference even a little smaller than for Ca.

Since the $5^1S - 5^3P_1$ intersystem line for Sr is at 6892A, whereas the corresponding transition for Ca is at 6572A, we could predict that these SrH band systems were to be found in the red region of the spectrum, probably beyond 6900A. Their description, together with the analysis of the BaH

[1] R. S. Mulliken and A. Christy, Phys. Rev. 38, 87 (1931).

bands given in the preceding paper, completes the body of data on the prominent band systems of the diatomic hydrides of all the elements in the second column of the periodic table.

Experimental Procedure

Practically the same experimental technique was employed in obtaining these SrH spectrograms as has been already described for the case of BaH. The only innovation was in the construction of the electrodes, and was due to the fact that the strontium metal was in the form of rather elongated crystals. Portions of these crystals were broken off, dipped in kerosene, and formed under high pressure into a small solid cylinder of the proper size with a stud protruding from one of its two flat surfaces. This stud of the metal was then made a rivet holding the Sr block on the flattened end of a length of $\frac{1}{8}''$ brass rod which fitted into one of the plugs of the arc chamber. From 10 to 20 of these small Sr electrodes had to be burned in the arc for each exposure.

The band spectra emitted by this arc consist principally of three groups of bands with main heads at 7020A, 7347A and 7508A, degrading toward the violet. The first group and the short wave-length half of the middle group were registered nicely on an Eastman 40 plate dyed with dicyanine. But even though the dicyanine has appreciable sensitivity out to beyond the SrH band line of longest wave-length at 7650A, this sensitivity proved insufficient to give an intense enough spectrogram of this long wave-length end with rather long exposure times. We noted that kryptocyanine has the maximum of its sensitivity curve at about 7500A, however, and with Eastman 40 plates dyed with kryptocyanine we obtained fairly intense spectrograms of this long wave-length portion of the spectrum. In addition to these bands in the red, there is a very dense grouping of lines in the yellow-green region which we have not investigated, and a rather intense small group of bands at 5800A which probably originate in some polyatomic molecule.

Before the measuring of the spectrograms of the red bands, it was observed that the groups at 7347A and 7508A had about the expected spacing and structural features of a $^2\Pi \rightarrow {}^2\Sigma$ system for SrH. The quantum analysis verified this tentative conclusion. With the aid of the combination differences for the $^2\Sigma$ state from this analysis, it was then possible to analyze the 7020A band and to show that it is the predicted $^2\Sigma \rightarrow {}^2\Sigma$ transition with the same lower state as the other system. Fig. 1 is a reproduction of the spectrograms showing these two SrH band systems.

Analysis of the $^2\Pi \rightarrow {}^2\Sigma$ (0, 0) Band

Guided by the intensity distribution among the lines of the 7508A band, and a rough idea of the probable magnitude of the spin doubling in the lower state, the assignment of lines and J values in the P_1, $^PQ_{12}$, Q_1 and $^QR_{12}$ branches proved to be a simple task. The proper designation of R_1 branch lines then followed from the combination differences between the other five branches of this group. The rather peculiar regularity of the spacing of the band lines to the long wave-length side of the $^2\Pi_{1/2}$ origin to be seen in Fig. 1

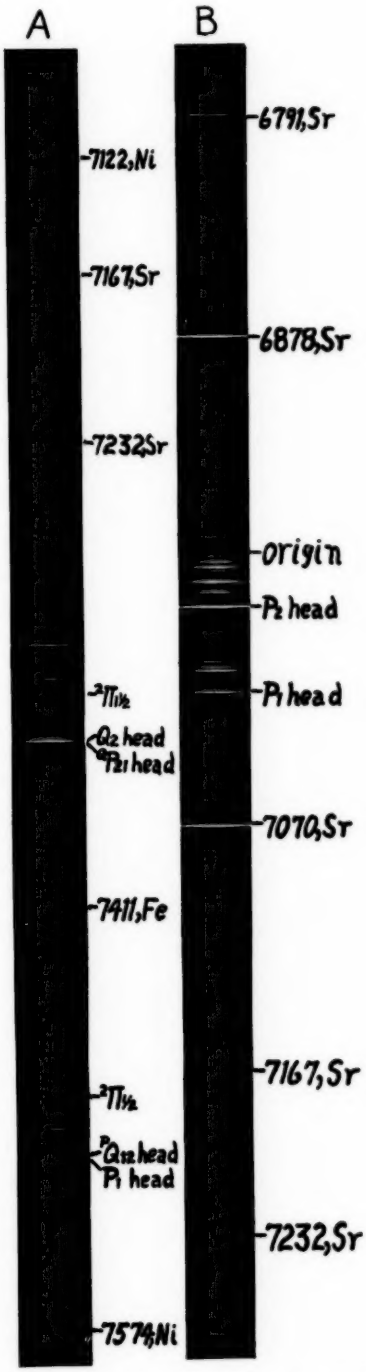

Fig. 1. Reproductions of spectrograms showing the SrH bands. *A*. $^2\Pi \rightarrow {}^2\Sigma$ band sequence. The $^0P_{12}$ branch proceeds out beyond the P_1 head, but the lines are of low intensity. The P_2 branch proceeds similarly towards longer wave-lengths from the Q_2 head, and does not form a head. The head just on the short wave-length side of the $^2\Pi_{1\ 1/2}$ origin belongs to the Q_2 branch of the (1, 1) band. *B*. $^2\Sigma \rightarrow {}^2\Sigma$ band sequence. Note that the head next to the P_1 head is not the P_2 head but rather is P_1 for the (1, 1) band. The large separation of the P_1 and P_2 heads is indicative of the record size of the doubling in the upper $^2\Sigma$ state.

is due to the interlacing of the P_1 and ${}^PQ_{12}$ branches. The double-headed appearance of the bands is not as evident as in the case of the BaH system because of the fact that these branches do not turn back.

In the 7347A group of branches the two strong heads would appear to belong to the P_2 and Q_2 branches respectively. But the relative distribution and form of the six branches in each sub-group of a $^2\Pi \rightarrow {}^2\Sigma$ band are always similar, and it was therefore concluded that the Q_2 branch produces the first head, the second being due to the Q_2 branch of the (1, 1) band. This arrangement proved to be correct, and with the aid of the various combination differ-

TABLE I. *Assignment of frequencies (cm^{-1}) for (0, 0) band of $^2\Pi \rightarrow {}^2\Sigma$ system of SrII (d indicates a double line).*

	$^2\Pi_{\frac{1}{2}} \rightarrow {}^2\Sigma$					
$J''+\frac{1}{2}$	${}^OP_{12}$	P_1	${}^PQ_{12}$	Q_1	${}^QR_{12}$	R_1
1			13357.77	13360.87	13362.50*d*	13377.83*d*
2	13339.43*d*	13357.64	56.36	62.50*d*	64.53	90.83
3	26.43*d*	56.07	55.00	64.23	66.50	404.07
4	13.84	54.59	53.70	66.07	68.54	17.27
5	01.31	53.13	52.45	68.01	70.66	30.25
6	288.91	51.76	51.23	70.05	73.03	43.47
7	76.65	50.44	50.07	72.17	75.33	56.56
8	64.52	49.10	48.94	74.42	77.83	69.64
9	52.58	47.85*d*	47.85*d*	76.77	80.36	82.66
10	40.73	46.64*d*	46.64*d*	79.24	83.13	495.69*d*
11	29.11	45.45	45.61	81.80	85.94	508.67*d*
12	17.71	44.24	44.57	84.52	88.95	21.41
13	206.46	43.03	43.48	87.38	91.99	34.20
14	195.40	41.83	42.40	90.41	95.20	46.93
15	84.56	40.66	41.32	93.46	398.58	59.53
16	73.99	39.43	40.22	396.76	402.09	72.00
17	63.62	38.20	39.13	400.09	05.71	84.38
18	53.48	36.94*d*	38.03	03.59	09.48	596.64
19	43.60	35.73*d*	36.94*dd*	07.27	13.39	608.75*d*
20	34.00	34.52*d*	35.73*d*	11.05	17.41	20.82
21	24.65	33.29*d*	34.52*d*	14.99	21.64	32.67
22	15.46	32.02	33.29*d*	19.07	25.94	44.40
23	106.72	30.72	32.14	23.30	30.40	55.94*d*
24	098.18	29.45	31.04	27.69	35.08	67.45
25	089.86	28.12	29.84	32.25	39.86	78.73
26		26.88	28.66	36.96	44.78	689.97
27		25.56	27.53	41.68	49.83	701.12
28		24.34*d*	26.43*d*	46.67	55.07	12.05
29		23.16	25.39	51.79	60.43	23.02
30		21.99	24.34*d*	57.03	65.98	
31		20.90*d*	23.32	62.49	71.59	
32		19.83	22.44	68.04	77.41	
33		18.86	21.78	73.79	83.37	
34		17.97	29.90*d*	79.67	89.50	
35		17.21	20.40	85.65	495.69	
36		16.50		91.95*d*	502.18	
37		15.92		498.20	08.67	
38		15.48		504.64	15.48	
39		15.24		11.28	22.29	
40				18.04	29.22	
41				24.99	36.23	
42				32.05		
43				39.24		
44				46.58		
45				54.07		
46				61.66		

TABLE I. (*Continued*).

$^2\Pi_{1\frac{1}{2}} \rightarrow {}^2\Sigma$						
$J''+\frac{1}{2}$	P_2	$^QP_{21}$	Q_2	$^RQ_{21}$	R_2	$^SR_{21}$
2			13644.83	13659.27	13663.12	13677.59
3	13622.66	13644.39	41.52	62.90	67.26	88.67
4	12.31	41.04	38.25	66.73	71.21	699.99*d*
5	601.89	37.64	35.10	70.68	75.32	711.26
6	591.53	34.53*d*	32.10	74.57	79.52	22.67
7	81.18	31.26	29.20	78.73	83.75	34.14
8	70.98	28.20	26.44	82.84	88.04	45.59*d*
9	60.91	25.36	23.87	86.98	92.44	57.03
10	51.00	22.66	21.28	91.23	696.86	69.18
11	41.09	20.06	19.06	95.57	701.38	81.13
12	31.41	17.66	16.97	699.99*d*	06.02	793.19
13	21.87	15.50	15.04	704.43	10.63	804.89
14	12.44	13.33*d*	13.33*d*	08.98	15.35	17.61
15	503.28	11.66	11.80	13.62	20.19	29.95
16	494.18	09.59	10.58	18.31	25.11	42.58
17	85.21	08.75*d*	09.59	23.02	30.09	55.25
18	76.56	07.39	08.75	27.94	35.15	68.11
19	68.04	06.53	08.16	32.88	40.28	81.09
20	59.70	05.87	07.92	37.90	45.59*d*	894.32
21	51.69	05.44	07.92	43.06	50.85	907.60
22	43.69	05.44	08.16	48.22	56.27	21.11
23	36.06	05.44	08.75	53.60	61.71	34.75
24	28.61		09.59	58.98	67.38	48.70
25	21.07		10.87	64.53	73.06	62.48
26	13.65		12.31	70.14	78.87	76.44
27	406.37		14.05	75.77	84.85	13990.79
28	399.25		16.11	81.68	90.79	14005.19
29			18.47	87.60	796.98	19.62
30			21.12	93.63	803.21	34.26
31			23.96	799.77	09.53	48.98
32			27.24	806.08	16.09	63.86
33			30.74	12.34	22.67	78.79
34			34.53	18.91	29.29	093.71
35			38.61	25.50	36.14	108.83
36			42.96	32.22	43.04	23.93
37			47.55	39.11	50.08	
38			52.51	46.15	57.08	
39			57.49	53.20		

ences mentioned in the discussion of the BaH spectrum, the assignments to the other branches were made. The wave numbers of all the lines of the twelve branches of this SrH band are given in Table I.

Fortrat diagrams of these $^2\Pi \rightarrow {}^2\Sigma$ bands of BaH and SrH of course show considerable similarity since the ratio A/B is somewhat the same for both. The most evident difference between the two is that the Q_1 branch lies much nearer to the P_1 branch than to the R_1 branch in the SrH diagram, whereas in the case of BaH the Q_1 branch is rather nearer the R_1 branch. This difference in the relative position of the Q_1 branch is due to the fact that the large Λ-type doubling in the $^2\Pi_{1/2}$ state is of opposite sign in the two bands.

EVALUATION OF THE CONSTANTS B, D AND A

The lower state combinations defined by Eq. (1) of the preceding paper from which the molecular constants are computed are listed in Table II. The last column of this table gives the average values from which the B_0'' and D_0'' given in Table IV were calculated from Eq. (3) of the BaH paper.

TABLE II. *Lower state combinations.* The 1st set of data gives the Δ_2F_1'' values obtained from Eq. (1) of preceding paper. The second set the $\Delta_2F_2''(J)$. The J values have been omitted in headings; $R_1-P_1=R_1(J-1)-P_1(J+1)$, etc. The $\Delta_2F''(K)$ values in the last column are the average of $\Delta_2F_1''(J=K+\frac{1}{2})$ and $\Delta_2F_2''(J=K-\frac{1}{2})$, used in Eq. (3).

	$\Delta_2F_1''(J)$				$\Delta_2F_2''(J)$					
$J''+\frac{1}{2}$	R_1-P_1	${}^SR_{21}-{}^QP_{21}$	av.	$J''+\frac{1}{2}$	R_2-P_2	${}^QR_{12}-{}^QP_{12}$	av.	K	$\Delta_2F''(K)$
2	21.76		21.76	2		36.07	36.07	1	21.76
3	36.24	36.55	36.40	3	50.81	50.69	50.75	2	36.15
4	50.94	51.03	50.98	4	65.37	65.19	65.28	3	50.81
5	65.51	65.46	65.49	5	79.68	79.63	79.65	4	65.36
6	79.81	80.00	79.90	6	94.14	94.01	94.07	6	79.71
7	94.37	94.47	94.42	7	108.54	108.51	108.52	6	94.25
8	108.71	108.78	108.75	8	122.84	122.75	122.80	7	108.62
9	123.00	122.93	122.96	9	137.04	137.10	137.07	8	122.62
10	137.21	136.97	137.09	10	151.35	151.25	151.30	9	137.08
11	151.45	151.52	151.49	11	165.45	165.42	165.43	10	151.39
12	165.64	165.63	165.63	12	179.51	179.48	179.50	11	165.53
13	179.58	179.86	179.72	13	193.58	193.55	193.56	12	179.60
14	193.54	193.23	193.38	14	207.35	207.43	207.39	13	193.47
15	207.50	208.02	207.76	15	221.17	221.21	221.19	14	207.43
16	221.33	221.20	221.27	16	234.98	234.96	234.97	15	221.24
17	235.06	235.19	235.12	17	248.55	248.61	248.58	16	235.00
18	248.65	248.72	248.68	18	262.05	262.11	262.08	17	248.60
19	262.12	262.24	262.18	19	275.45	275.48	275.46	18	262.09
20	275.46	275.65	275.55	20	288.59	288.74	288.67	19	275.46
21	288.80	288.88	288.84	21	301.90	301.95	301.92	20	288.73
22	301.95	302.16	302.05	22	314.79	314.92	314.85	21	301.93
23	314.99		314.99	23	327.66	327.76	327.71	22	314.90
24	327.82		327.82	24	340.64	340.54	340.59	23	327.75
								24	340.59

TABLE III. *Upper state combinations.* The Δ_2F'' headings are defined by Eq. (2) in preceding paper. $\Delta_2F_{1dc}(J)$ is the average of $\Delta_2F_{1c}(J)$ and $\Delta_2F_{1d}(J)$. $\Delta_2F_{2dc}(J)$ is the average of $\Delta_2F_{2d}(J)$, and $\Delta_2F_{2c}(J)$.

$J''+\frac{1}{2}$	$\Delta_2F_{1d}(J)$	$\Delta_2F_{1c}(J)$	$\Delta_2F_{1dc}(J)$	$J''+\frac{1}{2}$	$\Delta_2F_{2d}(J)$	$\Delta_2F_{2c}(J)$	$\Delta_2F_{2dc}(J)$
2	33.19	25.10	29.15	2			
3	48.00	40.07	44.03	3	44.60		44.60
4	62.68	54.70	58.69	4	58.90	58.95	58.93
5	77.12	69.35	73.24	5	73.43	73.62	73.52
6	91.71	84.12	87.41	6	87.99	88.14	88.07
7	106.12	98.68	102.40	7	102.57	102.88	102.72
8	120.54	113.31	116.93	8	117.06	117.39	117.23
9	134.81	127.78	131.30	9	131.53	131.67	131.60
10	149.05	142.40	145.72	10	145.86	145.52	146.19
11	163.22	156.83	160.02	11	160.29	161.07	160.78
12	177.17	171.24	174.21	12	174.61	175.53	175.07
13	191.17	185.53	188.35	13	188.76	189.39	189.08
14	205.12	199.80	202.46	14	202.91	204.28	203.60
15	218.87	214.02	216.45	15	216.91	218.29	217.60
16	232.57	228.10	230.33	16	230.93	232.99	231.96
17	246.18	242.09	244.14	17	244.88	246.50	245.69
18	259.70	256.00	257.85	18	258.59	260.72	259.66
19	273.02	269.79	271.40	19	272.24	274.56	273.40
20	286.30	283.41	284.86	20	285.89	288.45	287.17
21	299.38	296.99	298.18	21	299.16	302.16	300.66
22	312.38	310.48	311.43	22	312.58	315.67	314.12
23	325.22	323.68	324.45	23	325.65	329.31	327.48
24		336.90		24	338.77		
25		350.00		25	351.99		

This value of $B_0''=3.6198$ corresponds to an internuclear distance of 2.16×10^{-8} cm. Table III contains the combinations as defined by Eq. (2) for the

$^2\Pi$ state. Again the average values listed in the columns headed $\Delta_2F_{dc}(J)$ and defined by Eq. (4) were used in calculating the B_0' and D_0' constants.[2] These constants are given in Table IV.

Calculation of the coupling constant A for the $\Lambda\Sigma$ interaction using the Hill and Van Vleck equation gives $A=299$. This value stands to the coupling

TABLE IV. *Constants from the quantum analysis of the SrH bands (cm^{-1} units).*

Normal $^2\Sigma$ state:	$B_0''=3.6198$, $D_0''=-1.287\times10^{-4}$, $r_0=2.16\times10^{-8}$ cm
	$\gamma_0=+0.122$
$^2\Pi$ state:	$B_{0,-1/2}'=3.6683$, $D_{0,-1/2}'=-1.33\times10^{-4}$
	$B_{0,+1/2}'=3.6787$, $D_{0,+1/2}'=1.13\times10^{-4}$
	$A=299$, $p_0=-3.92$, $q_0=-0.398$
Upper $^2\Sigma$ state:	$B_0'=3.8318$, $D_0'=-1.641\times10^{-4}$, $\gamma_0'=-3.81$

constant $A=387$ for the lowest ^3P state of the strontium atom in practically the same ratio as exists between the A's for the corresponding $^2\Pi$ state of CaH and the lowest ^3P state of Ca.

ANALYSIS OF THE 7020A $^2\Sigma\rightarrow{}^2\Sigma$ (0, 0) BAND OF SrH

There are eight series of lines or branches in the 7020A band, four of which belong to the (0,0) and the other four to the (1, 1) vibrational transition. Assuming that the branch forming the first head on the red end is the P_1 of the (0, 0) band, that series which with this P_1 branch gives the same lower state combinations $\Delta_2F_1''(J)$ as previously found for the $^2\Pi\rightarrow{}^2\Sigma$ band was designated as the corresponding R_1 branch. Then knowing exactly the doubling in the normal $^2\Sigma$ state, those two of the remaining six series which give the same $\Delta_2F_2''(J)$ combination differences as found above for the $^2\Pi\rightarrow{}^2\Sigma$ band could be labelled the P_2 and R_2 branches. The assignment of wave numbers for these four branches is given in Table V. The R_2 branch is relatively quite weak, and we can follow it only to $J=15\frac{1}{2}$ on our spectrograms. This may be due to the fact that the sensitivity of the dicyanine dye is beginning to decrease a little in this wave-length region.

The second head of this 7020A band to be seen in Fig. 1 is not formed by the P_2 branch, as one would at first suppose, but is rather the P_1 head of the (1, 1) band. The large separation of the P_1 and P_2 branch heads indicates a very large spin doubling in the upper $^2\Sigma$ state (cf. next section). Providing the doubling in both of the electronic states involved is sufficiently large, weak Q_{21} and Q_{12} branch lines are expected near the origin as satellites of the P and R lines in bands of this type. The evidence for their existence in this band is not very good, however. There is a line that could be designated $Q_{21}(\frac{1}{2})$ about 6 cm^{-1} to the high frequency side of $R_1(\frac{1}{2})$ as it should be, but it is obviously a double or triple line. The other Q_{21} and Q_{12} lines are probably too close to the R_2 and P_1 lines respectively to be resolved on our spectrograms.

Table VI contains the lower state combination differences for this band. The values are practically identical with those of the $^2\Pi\rightarrow{}^2\Sigma$ band given in

[2] Evaluation of $B_{0,-1/2}'$ from the Δ_2F_{1c} and Δ_2F_{1d} values separately gives $B_{0,-1/2,c}'=3.5206$ and $B_{0,+1/2,d}'=3.8231$.

TABLE V. *Assignment of frequencies for the 7020A $^2\Sigma \rightarrow {}^2\Sigma$ (0, 0) band of SrH (d indicates a double line; cm^{-1} units).*

$J+\frac{1}{2}$	P_1	R_1	P_2	R_2
1		14357.81		14373.71*d*
2	14345.30	363.79		384.20*d*
3	336.01	370.78	14337.52	395.00*d*
4	327.14	376.93	333.74*d*	406.30
5	319.60	384.20	329.95	417.83
6	311.54	391.73	326.66	429.66
7	304.31	399.71	323.75	441.86
8	297.44	408.03	321.19	454.37
9	290.92	416.79	319.00	467.12
10	285.01	425.90	317.28	480.17
11	279.45	435.26	315.85	493.48
12	274.35	445.08	314.80	507.06
13	269.63	455.24	314.25	520.83
14	265.32	465.72	313.82	534.90
15	261.52	476.50	313.47	548.76
16	258.06	487.62	313.82	563.45
17	255.04	498.99	314.25	
18	252.35	510.64	314.80	
19	250.22	522.64	314.80	
20	248.45	534.80	315.85	
21	247.03	547.29	317.28	
22	246.00	559.98	319.06	
23	245.27	572.90	321.19	
24	244.99	586.03	323.77	
25	244.99	599.38	326.66	
26	245.27	612.86	329.42	
27	246.00	626.48	332.18	
28	247.03	640.26	335.16	
29	248.45	654.21	338.62	
30	250.23	668.26	342.20	
31	252.35		346.03	
32	254.48		350.20	
33	257.02		354.58	
34	259.86		359.02	
35	262.85		363.79	
36	266.04		368.66	
37	269.63		373.71	
38	273.34		378.90	
39	277.33		384.20	
40	281.41		389.55	
41	285.71		395.00	
42	290.09		400.50	
43	294.46		406.30	
44	299.18		412.17	

Table II, showing that the two systems have the same normal $^2\Sigma$ state. The initial state combinations are given by the relations

$$R_1(J) - P_1(J) = F_1'(J+1) - F_1'(J-1) = \Delta_2 F_1'(J)$$
$$R_2(J) - P_2(J) = F_2'(J+1) - F_2'(J-1) = \Delta_2 F_2'(J).$$

These values are also listed in Table VI. There is a large divergence between the values of $\Delta_2 F_1'$ and $\Delta_2 F_2'$ due to very large spin doubling. In fact this doubling is the largest yet found for any $^2\Sigma$ state. Nevertheless, as in the case of the lower $^2\Sigma$ state, if we represent by $T_1(K)$ the levels with $J=K+\frac{1}{2}$ and by $T_2(K)$ the levels with $J=K-\frac{1}{2}$, then $T'(K)=\frac{1}{2}\{T_1(K)+T_2(K)\}$ has the value

$$T(K) = T_0 + T_v + B'[K(K+1) - G^2] + D'K^2(K+1)^2 + \tfrac{1}{2}\gamma$$

TABLE VI. *Upper and lower state combinations of 7020A* $^2\Sigma \rightarrow {}^2\Sigma$ *band.* The $\Delta_2F(K)$ values are the average of the second and third columns in each set, and are the ΔF values from which the constants are calculated.

Lower state combinations					Upper state combinations				
$J''+\frac{1}{2}$	R_1-P_1	R_2-P_2	K	$\Delta_2F''(K)$	$J+\frac{1}{2}$	$R_1(J)$ $-P_1(J)$	$R_2(J)$ $-P_2(J)$	K	$\Delta_2F(K)$
2	21.80	36.19	1	21.80	2	18.49		1	
3	36.65	50.46	2	36.42	3	34.17	57.48	2	
4	51.12	65.05	3	50.79	4	49.79	72.56	3	53.63
5	65.39	79.64	4	65.22	5	65.14	87.88	4	68.85
6	79.89	94.08	5	79.76	6	80.19	103.00	5	84.04
7	94.29	108.47	6	94.18	7	95.40	118.11	6	99.20
8	108.79	122.86	7	108.63	8	110.59	133.18	7	114.35
9	123.02	137.09	8	123.94	9	125.87	148.12	8	129.52
10	137.34	151.29	9	137.22	10	140.89	162.89	9	144.51
11	151.55	165.37	10	151.42	11	155.81	177.63	10	159.35
12	165.63	179.23	11	165.50	12	170.73	192.26	11	174.18
13	179.76	193.24	12	179.50	13	185.61	206.58	12	188.94
14	193.72	207.36	13	193.48	14	200.40	221.08	13	203.49
15	207.66	221.08	14	207.51	15	214.98	235.29	14	218.03
16	221.46	234.51	15	221.27	16	229.56	249.63	15	232.42
17	235.27	248.65	16	234.89	17	243.95			
18	248.77		17	248.71	18	258.29			
19	262.19				19	272.42			
20	275.61				20	286.35			
21	288.80				21	300.26			
22	302.02				22	313.98			
23	314.99				23	327.63			
24	327.91				24	341.04			
25	340.76				25	354.39			
26	353.38				26	367.59			
27	365.83				27	380.48			
28	378.03				28	393.23			
29	390.03				29	405.76			
30	401.86				30	418.03			
31	413.78								

and

$$\Delta_2F'(K) = B'(4K + 2) + D'(8K^3 + 12K^2 + 12K + 4).$$

The $\Delta_2F'(K)$ values are given in the last column of Table VI. These have been used to compute the B_0 and D_0 constants for this upper $^2\Sigma$ state given in Table IV.

SPIN DOUBLING IN THE $^2\Sigma$ STATES AND Λ-TYPE DOUBLING IN THE $^2\Pi$ STATE OF THE SrH BANDS

These bands offer an interesting example, very similar to that of CaH, for the application of the theory of spin and Λ-type doubling. Fig. 2 exhibits the spin doublings in both of the $^2\Sigma$ states of SrH, as well as the Λ-type doubling in the $^2\Pi_{1/2}$ $^2\Pi_{11/2}$ levels. The computations for these curves were carried out in exactly the same way as outlined in the preceding paper, and the values of the doubling constants γ, p, and q given in Table IV have been calculated using equations (5) and (6). The change of slope of the spin doubling curve for the upper $^2\Sigma$ state, just as for the corresponding state of CaH, is probably due to the perturbing effect of other near-lying levels. Fig. 3 shows the relative spacing of the four terms of the $^2\Pi$ states with increasing K, $T_{1d}(J)$ being

taken as zero. Comparing this figure with the corresponding diagram in the preceding paper, we note that the separation of the T_2 levels is greater for SrH than for BaH, indicating that this $^2\Pi$ state of BaH is much closer to case *a*. The separation of the T_1 levels is greater for SrH than for the corresponding levels of either CaH[1] or BaH because of the large interaction with the near-lying upper $^2\Sigma$ state. But nevertheless these two levels begin to approach each other at $K'=28$, showing that transition towards case *b* is setting in.

It is to be noted that all the doubling constants except γ_0 for the normal $^2\Sigma$ state are negative. The fact that the p_0 and q_0 of the $^2\Pi$ state are negative

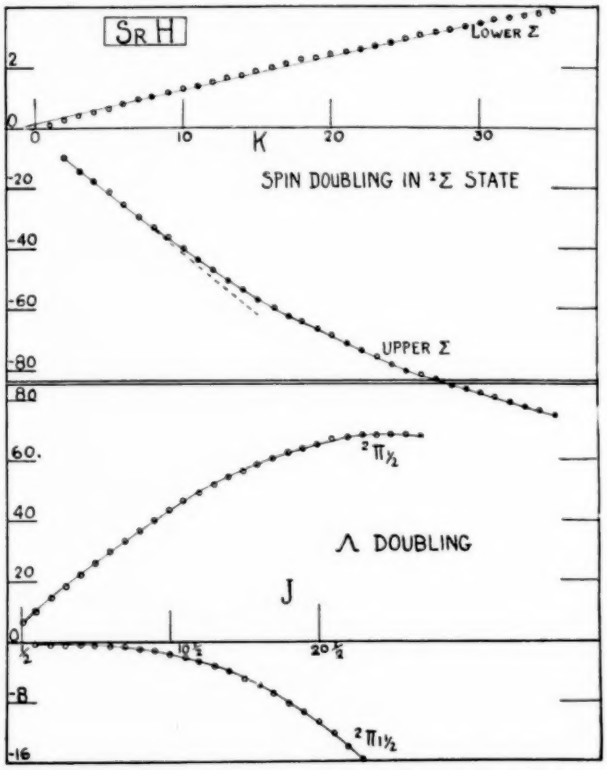

Fig. 2. Spin and Λ-type doublings in the SrH states. Note particularly the change in slope of the spin doubling curve for the upper $^2\Sigma$ state as compared to the usual linear relation holding for the normal $^2\Sigma$ state, and the tendency for the Λ-type doubling in the $^2\Pi_{1/2}$ state to finally begin to decrease as J becomes large showing the setting-in of a transition towards case *b*.

indicates interaction with a $^2\Sigma^+$ state above it, and that this interaction is with the observed upper $^2\Sigma$ state is attested by the near equality of this $p_0 = -3.92$ with the $\gamma_0 = -3.81$ for the $^2\Sigma$ state as well as by the size of these quantities. For the similar $^2\Pi$ state of BaH where there is no such near $^2\Sigma$ state above it, we have shown that the constants p_0 and q_0 are positive and much smaller in value. And calculation with the formulas for $\gamma = p$ and for q assuming pure precession between these two SrH states (Equations (8) of the preceding paper), with A and B as given in Table IV, $l=1$, and $\nu(\Pi, \Sigma)$

$= -850$ (the difference in cm^{-1} between the mean of the II levels and the upper $^2\Sigma$ level), gives $\gamma = p = -5.18$ and $q = -0.63$.

These relations between these SrH states demonstrate that a very considerable amount of l-uncoupling takes place with increase of the molecular rotation, as is also true for the corresponding CaH states.[1,3] Setting the doublet interval of the upper $^2\Sigma$ level equal to $A\rho$, where ρ is the component of l in the direction of K, we compute that at $K = 35$ $\rho = 95/299 = 0.32$. For the $^2\Pi_d$ levels, then, the doublet interval for large K should become much larger than that calculated according to the Hill and Van Vleck equation, while the interval between the $^2\Pi_e$ levels should asymptotically approach zero as K increases.[1] If our data for the doubling in the SrH $^2\Pi$ state extended to higher K

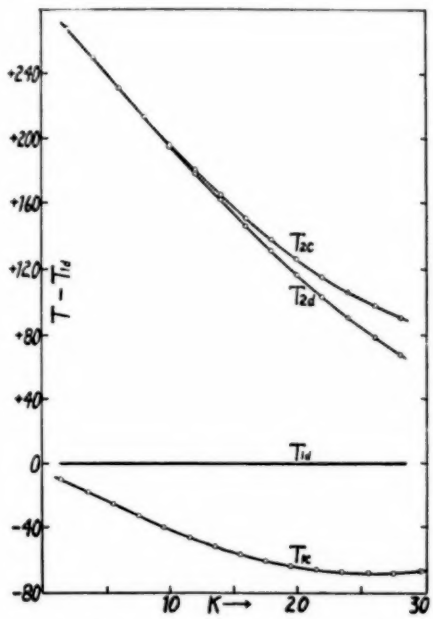

Fig. 3. Relative separations of the term values for the $^2\Pi$ state of SrH, $T_{1d}(J)$ being taken as zero. Compare the similar diagrams for CaH (reference 1) and for BaH (preceding paper).

values, we would expect to see this behavior of the II levels about as well illustrated as for CaH, for the comparison of our Fig. 3 with the similar plot for CaH[4] shows the same trends occurring with increasing K.

Discussion

In view of the low energy of the lowest ^3D levels in Ca, Sr and Ba and the relative position of this ^3D and the ^3P in these atoms and that of the $^2\Pi$ and upper $^2\Sigma$ states (assuming the indicated BaH band farther into the red to be $^2\Sigma$, $^2\Sigma$) in CaH, SrH and BaH, it is tempting to consider the normal state to be $\cdots np\sigma$ and the upper $^2\Sigma$ to be $\cdots (n-1)d\sigma$. However, the same argu-

[3] W. W. Watson, Phys. Rev. **39**, 278 (1932).
[4] Reference 1, Fig. 4.

ments that led Mulliken and Christy[1] to interpret the upper $^2\Sigma$ state of CaH as $\cdots 4p\sigma$ hold for SrH. For, as we have shown above, the equality of the doubling constants p_0 for the $^2\Pi$ state and γ_0 for the upper $^2\Sigma$ state and their close agreement with the calculated values assuming a relation of pure precession with $l=1$ makes it highly probable that this relation exists between these two states. Therefore these two states are to be considered as $\cdots 5p\pi$ and $\cdots 5p\sigma$ respectively, which leaves $\cdots 4d\sigma$ as the possible electron configuration for the normal $^2\Sigma$ state.

It is necessary to attribute the fact that $np\sigma$ lies above $np\pi$ to a quantum mechanical repulsion between the normal $(n-1)d\sigma$ and the $np\sigma$ states. Also this interpretation predicts a $\cdots (n-1)d\pi$ $^2\Pi$ state which must lie higher than the $\cdots np\pi$, $^2\Pi$ state, for if it were lower the interaction with the normal state would produce a considerably larger γ_0 in the latter than is observed. Possibly there may be bands for CaH and SrH involving this $\cdots (n-1)d\pi$, $^2\Pi$ and a $\cdots (n-1)d\delta$, $^2\Delta$, with perhaps close approach to case d' conditions, and lying farther into the ultraviolet than heretofore investigated. It may be too that the dissociation relations for all these states are complicated, as was suggested in the preceding paper as a really necessary assumption for the BaH states in view of their observed constants.

We wish to thank Dr. Alden J. King for the generous supply of pure strontium metal placed at our disposal, and we are indebted to Professor R. S. Mulliken for helpful correspondence on the subject of the nature of the probable electronic configurations.

FINE STRUCTURE OF THE VISIBLE ABSORPTION BANDS OF BROMINE

By Weldon G. Brown*
Ryerson Physical Laboratory, University of Chicago

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Abstract

A group of bands (from $v'=7$ to $v'=13$, $v''=2$, 3 and 4) in the main absorption band system of bromine ($Br_2^{79,81}$) have been analyzed and found to consist of P and R branches only. Branches of the less abundant molecules, Br_2^{79} and Br_2^{81}, showing alternating intensities, have been identified in several cases but owing to insufficient resolution a quantitative determination of the ratio of intensities has not been possible. An accurate calculation of the vibrational isotope shift of band origins has confirmed the quantum numbering previously deduced by the writer from measurements of band heads. The numerical values of the vibrational constants have been revised slightly from data on band origins. The analysis gave the following rotational constants for the $Br_2^{79,81}$ molecule:

$B_e''=0.08091$	$B_e'=0.0596$
$\alpha_e''=0.00028$	$\alpha_e'=0.00062$
$I_e''=342.1\times10^{-40}$	$I_e'=465\times10^{-40}$
$r_e''=2.28\times10^{-8}$	$r_e'=2.65\times10^{-8}$

Introduction

THE analysis of the visible absorption bands of iodine and chlorine has made it possible to predict with reasonable certainty that the corresponding bands of bromine have the same simple structure, namely, P and R branches only. Nevertheless this spectrum up to the present has defied analysis,[1] for in spite of the smaller atomic weight the bands are more complicated in appearance than those of iodine. This complex appearance is due primarily to the unique isotope situation. The two equally abundant atomic isotopes,[2] 79 and 81, giving rise to three molecular isotopes, $Br_2^{79,79}$, $Br_2^{79,81}$ and $Br_2^{81,81}$ in the relative abundance 1:2:1. The relative masses are such that the vibrational isotope shifts are small so that each band in the spectrum is made up of a superposition of three bands each having one P and one R branch.

The vibrational analysis of these bands was first studied by Kuhn.[3] Recently the vibrational isotope shift of band heads was observed by the writer[4] and used to establish the quantum numbering. In the latter work a second and weaker band system lying in the extreme red was observed. The extreme red bands, important for the development of theory of the electronic states of the halogens,[5] have not yet been analyzed.

* National Research Fellow.

[1] M. Hay, J. Franklin Inst. **208**, 363 (1929). The dispersion employed in this work was insufficient to resolve the $P-R$ doubling.

[2] F. W. Aston, Proc. Roy. Soc. **115**, 487 (1927), gives 78.929 and 80.926 for the isotope masses. Chemical atomic weight 79.92.

[3] H. Kuhn, Zeits. f. Physik **39**, 77 (1926).

[4] W. G. Brown, Phys. Rev. **38**, 1179 (1931).

[5] R. S. Mulliken, Phys. Rev. **36**, 669, 1440 (1930).

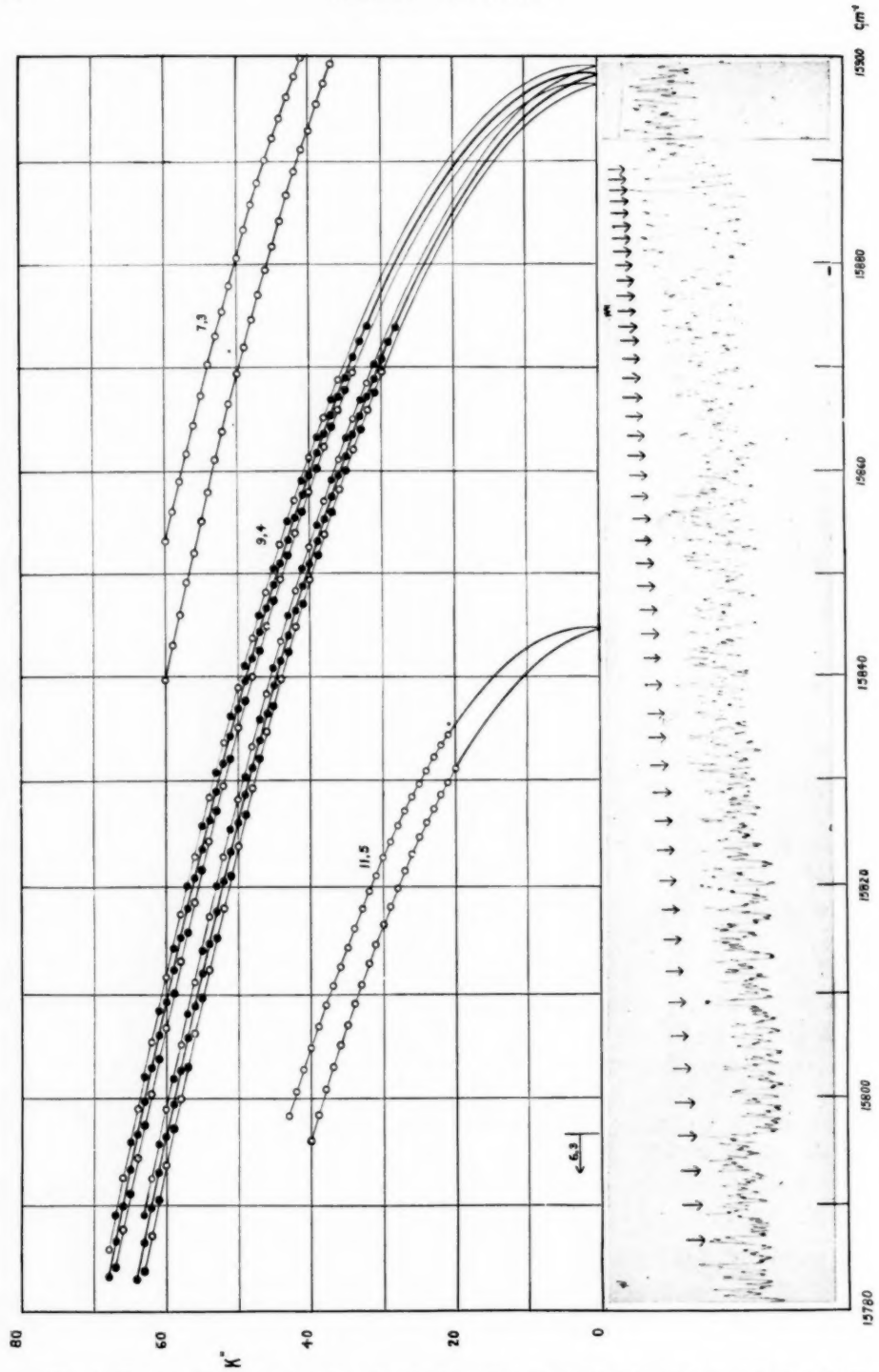

Fig. 1. Fortrat diagram showing the six branches of the 9,4 band but only the $Br_2^{79,81}$ branches of the weaker overlapping bands, 11,5, and 7,3. The arrows indicate the $P-R$ doublets of $Br_2^{79,81}$ (9,4). Alternating intensities are indicated by light and dark circles.

Experimental

The photographs were taken in the third order of a 21 ft. Rowland grating (0.8A/mm) on Ilford Special Rapid Panchromatic Plates with neon lines as standards. Two Pyrex absorption tubes, 50 and 150 cm in length were used, the longer tube for the weaker bands in the red. The lines are quite sensitive to pressure broadening and it was found necessary to employ vapor pressures of less than 100 mm to obtain satisfactory resolution. With a single filament 120 watt tungsten lamp exposures from six to twelve hours sufficed depending on the vapor pressure.[6] No particular precautions were taken to ensure purity of the bromine beyond two fractional distillations of reagent quality bromine in vacuum.

The measurements were reduced directly to wave numbers in vacuum by linear interpolation over intervals of 5 mm on the plate, a polynomial fitting wave-lengths of the standard lines being used to calculate frequencies for each 5 mm. For this time saving method of reduction the writer is indebted to Dr. W. Weizel. In the region 6000–6300A approximately 2,500 lines were measured.

In most cases the P and R branches of $Br_2^{79,81}$ were readily recognizable because of their slightly greater intensity and absence of alternation. Extensive use was made of the scheme devised by Loomis and Wood[7] for locating branches of the less abundant molecules. A characteristic feature of these bands is that the P and R branches of each molecule are coincident or form a series of close doublets over their entire course, $P(J)$ being coincident with or close to $R(J+4)$. The separation of these lines decreases with decreasing quantum number and in no case was it possible to resolve them for $P(J) <$ 18. In one case (*9,2*) they appear to be exactly coincident up to at least $J =$ 60 forming a single series of remarkably sharp lines. In some bands, *10,4* and *9,3*, the coincidence is not exact and results in broadening or smearing of lines. This so-called P-R doubling, of no theoretical significance, arises merely from the particular values of the constants and is characteristic also of the corresponding chlorine and certain of the iodine bands.

Calculation of Rotational Constants

The combination differences needed for calculating rotational constants are $R(J)-P(J)=\Delta_2F'(J)$ and $R(J-1)-P(J+1)=\Delta_2''F(J)$. These are listed (for $Br_2^{79,81}$) in Tables Ia and Ib so as to allow comparison of data for each vibrational level. The agreement is satisfactory in all cases where the P-R doubling has been resolved. Fortunately, in this case the calculation of the constants B' and B'' from the combination differences is an extremely simple one since they are given by

$$\Delta_2F = 2B + 4BJ + 8DJ^3$$

where the coefficient D is so small for both upper and lower states that one

[6] Weak continuous absorption overlaps the main absorption bands. Note the gradually changing background density in the microphotometer trace in Fig. 1.

[7] F. W. Loomis and R. W. Wood, Phys. Rev. **32**, 223 (1928).

TABLE Ia. *Combination differences for the lower levels of* $Br_2^{79,81}$. $\Delta_2F'' = R(J-1) - P(J+1)$

J	8,2	9,2	10,2	7,3	8,3	10,3	11,3	12,3	13,3	9,4	10,4	11,4
20		6.52			6.55							
21		6.83			6.94							
22		7.18			7.17							
23		7.51			7.51		7.51	7.53			7.55	
24	7.80	7.84			7.81		7.87	7.80	7.83		7.85	7.84
25	8.20	8.17			8.11		8.22	8.14	8.17		8.19	8.08
26	8.49	8.49			8.38		8.45	8.56	8.47		8.53	8.44
27	8.86	8.83	8.84		8.72		8.75	8.79	8.78		8.74	8.75
28	9.11	9.15	9.13		9.10		9.18	9.12	9.09		9.05	9.06
29	9.45	9.48	9.42		9.41		9.46	9.42	9.44		9.40	9.48
30	9.78	9.80	9.83		9.72		9.74	9.80	9.70		9.71	9.77
31	10.07	10.11	10.07		10.06		10.10	10.08	10.02		9.97	10.07
32	10.42	10.42	10.42		10.29		10.43	10.38	10.37		10.30	10.41
33	10.77	10.73	10.72		10.72		10.78	10.69	10.67	10.71	10.74	10.73
34	10.98	11.04	11.07		11.00		11.07	11.07	11.05	11.02	11.04	11.03
35	11.30	11.36	11.39		11.36	11.32	11.37	11.32	11.39	11.36	11.35	11.36
36	11.69	11.68	11.68		11.68	11.65	11.68	11.65	11.71	11.66	11.67	11.70
37	12.10	12.01	12.02		11.97	12.00	12.00	12.03	12.03	11.97	12.02	11.96
38	12.33	12.32	12.38		12.31	12.29	12.31	12.29	12.33	12.26	12.34	12.24
39	12.62	12.64	12.70		12.51	12.61	12.62	12.58	12.68	12.58	12.67	12.57
40	13.01	12.98	12.99		12.90	12.94	12.95	12.97	12.96	12.88	12.97	12.79
41		13.30	13.31		13.22	13.24	13.28	13.31	13.25	13.23	13.27	13.23
42		13.62	13.62		13.65	13.55	13.62	13.58	13.56	13.52	13.59	13.51
43		13.93	13.92		13.83	13.88	13.86	13.97	13.89	13.86	13.94	13.84
44		14.25	14.28			14.23	14.20	14.19	14.24	14.20	14.18	
45		14.60	14.61			14.60	14.56	14.50	14.52	14.45	14.49	
46		14.91	14.92			14.87	14.88	14.82	14.87	14.85	14.83	
47		15.23	15.24				15.24	15.20	15.20	15.09	15.20	
48		15.55	15.67					15.55		15.43	15.53	
49		15.88	15.88					15.82		15.73	15.78	
50		16.22	16.23					16.13		15.96	16.19	
51		16.52						16.41		16.40		
52		16.83						16.80		16.66		
53		17.15								16.97		
54		17.46								17.33		
55		17.77		17.77						17.64		
56				18.06						17.99		
57				18.36						18.37		
58				18.67						18.64		
59				18.99						18.88		
60				19.33						19.24		
61				19.61								
B'' obs.	0.08010	0.08017	0.08023	0.07998	0.07975	0.07988	0.08007	0.07995	0.07997	0.07967	0.08000	0.07975
B'' calc.		0.08022				0.07995					0.07967	

can use the theoretical value ($D_e = -4B_e^3/\omega_e^2$). The value of B is then obtained from the expression

$$B = \frac{\Sigma(\Delta_2F + 8DJ^3)}{4\Sigma(J + \frac{1}{2})}.$$

The values so obtained are shown in Table I together with the values calculated from an expression of the type

$$B_v = B_e - \alpha(v + \tfrac{1}{2}).$$

THE ISOTOPE EFFECT

The lines of the v', v'' band of $Br_2^{79,81}$ can be represented by the equation

$$\nu = \nu^0 + B_{v'}(J' + \tfrac{1}{2})^2 + D_{v'}(J' + \tfrac{1}{2})^4 - B_{v''}(J'' + \tfrac{1}{2})^2 - D_{v''}(J'' + \tfrac{1}{2})^4 \quad (1)$$

where the coefficients B_v and D_v are functions of the vibrational quantum numbers v' and v''

$$B_v = B_e - \alpha(v + \tfrac{1}{2}) \quad (2)$$

$$D_v = D_e + \beta(v + \tfrac{1}{2}). \quad (3)$$

TABLE IB. *Combination differences for the upper levels of* $Br_2^{79,81}$, $\Delta_2F' = R(J) - P(J)$

J	7,3	8,2	8,3	9,2	9,4	10,2	10,3	10,4	11,3	11,4	12,3	13,3
22			4.91									
23		5.08	5.06	5.02				5.04	4.95	4.98	4.85	4.75
24		5.35	5.32	5.17				5.24	5.20	5.10	5.06	4.94
25		5.51	5.45	5.45				5.44	5.35	5.32	5.31	5.22
26		5.78	5.65	5.71		5.62		5.69	5.54	5.52	5.48	5.40
27		5.98	5.94	5.86		5.83		5.90	5.78	5.75	5.73	5.59
28		6.17	6.15	6.12		6.04		6.00	5.93	5.97	5.89	5.83
29		6.34	6.37	6.33		6.27		6.24	6.21	6.15	6.11	5.95
30		6.60	6.62	6.46		6.40		6.45	6.44	6.48	6.27	6.16
31		6.77	6.71	6.73		6.66		6.62	6.63	6.70	6.53	6.41
32		6.99	7.03	6.94	6.99	6.84		6.92	6.86	6.86	6.70	6.60
33		7.29	7.23	7.16	7.21	7.09		7.15	7.05	7.08	6.91	6.82
34		7.52	7.48	7.35	7.41	7.28	7.30	7.34	7.28	7.29	7.13	7.04
35		7.60	7.68	7.57	7.65	7.48	7.50	7.57	7.47	7.48	7.33	7.29
36		7.85	7.91	7.77	7.89	7.74	7.73	7.83	7.60	7.64	7.55	7.48
37		8.09	8.16	8.00	8.07	7.96	7.93	7.99	7.81	7.87	7.73	7.66
38		8.39	8.25	8.23	8.25	8.15	8.14	8.20	8.07	8.09	7.92	7.88
39		8.58	8.53	8.43	8.44	8.37	8.34	8.45	8.28	8.21	8.14	8.06
40		8.73	8.74	8.75	8.69	8.54	8.56	8.66	8.47	8.46	8.35	8.27
41		8.93	8.99	8.87	8.86	8.78	8.77	8.87	8.69	8.62	8.56	8.45
42			9.16	9.03	9.12	9.02	8.95	9.08	8.90	8.88	8.79	8.63
43			9.50	9.32	9.36	9.18	9.19	9.24	9.08	9.06	9.00	8.83
44			9.59	9.45	9.51	9.36	9.44	9.47	9.26	9.31	9.16	9.03
45				9.69	9.75	9.63	9.65	9.66	9.49		9.34	9.31
46				9.99	9.93	9.88	9.86	9.88	9.75		9.60	9.47
47				10.09	10.20	10.05	10.06	10.11	9.93		9.82	9.63
48				10.41	10.35	10.27		10.34	10.16		10.03	9.87
49				10.67	10.56	10.57		10.59			10.19	
50				10.77	10.81	10.61		10.76			10.34	
51				11.05	11.01	10.90		11.02			10.59	
52				11.20	11.20						10.81	
53				11.36	11.41						11.04	
54	11.91			11.70	11.60							
55	12.14			11.86	11.87							
56	12.39			12.03	12.12							
57	12.58			12.32	12.30							
58	12.77				12.49							
59	12.99				12.73							
60	13.20				12.88							
61	13.45				13.13							
62	13.62											
B' obs.	0.05487	0.05412	0.05415	0.05355	0.05367	0.05297	0.05303		0.05250	0.05252	0.05170	0.05100
B' calc.	0.05487		0.05425		0.05362		0.05300		0.05237		0.05175	0.05112

The general theory [8] of the isotope effect in band spectra indicates that for an isotope molecule one substitutes $\rho(v+\frac{1}{2})$ for $(v+\frac{1}{2})$ and $\rho(J+\frac{1}{2})$ for $(J+\frac{1}{2})$ where ρ is the square root of the ratio of the reduced masses. ν° is also a function of the vibrational quantum numbers and so the isotope molecule will have a different origin, $\nu^\circ+\delta\nu^\circ$. $\delta\nu^\circ$ is the vibrational isotope effect and can be treated separately. Then on making these substitutions one finds that for the isotope molecule, such as Br_2^{79} or Br_2^{81}, one obtains new coefficients in equation (1) related to the original ones as follows:

$$^iB_v = [B_e - \alpha\rho(v+\tfrac{1}{2})]\rho^2 \quad (4)$$

$$^iD_v = [D_e + \beta\rho(v+\tfrac{1}{2})]\rho^4. \quad (5)$$

In table II the combination differences for Br_2^{79} and Br_2^{81} are given together with the B values calculated from them, and those calculated from the data for $Br_2^{79,81}$ by means of equation (4). The values of ρ calculated from Aston's[2] atomic weights, are 1.00623 and 0.99373 for Br_2^{79} and Br_2^{81} respectively.

Substituting appropriate values for the constants in equation (1) one can calculate from each band line a value of ν°. The origins calculated from Br_2^{79}

[8] R. S. Mulliken, Phys. Rev. **25**, 119 (1925).

or Br_2^{81} lines will differ from the corresponding $Br_2^{79,81}$ origins by an amount, $\delta\nu^\circ$ which is given theoretically by

$$\delta\nu^0 = \omega_e'(v' + \tfrac{1}{2})(\rho - 1) - \omega_e' x_e'(v' + \tfrac{1}{2})^2(\rho^2 - 1) + \cdots$$
$$- \omega_e''(v'' + \tfrac{1}{2})(\rho - 1) + \omega_e'' x_e''(v'' + \tfrac{1}{2})^2(\rho^2 - 1) - \cdots \qquad (6)$$

where the vibrational constants ω_e and x_e to be used are those for $Br_2^{79,81}$ and the appropriate values of ρ are to be substituted to obtain the shift of the

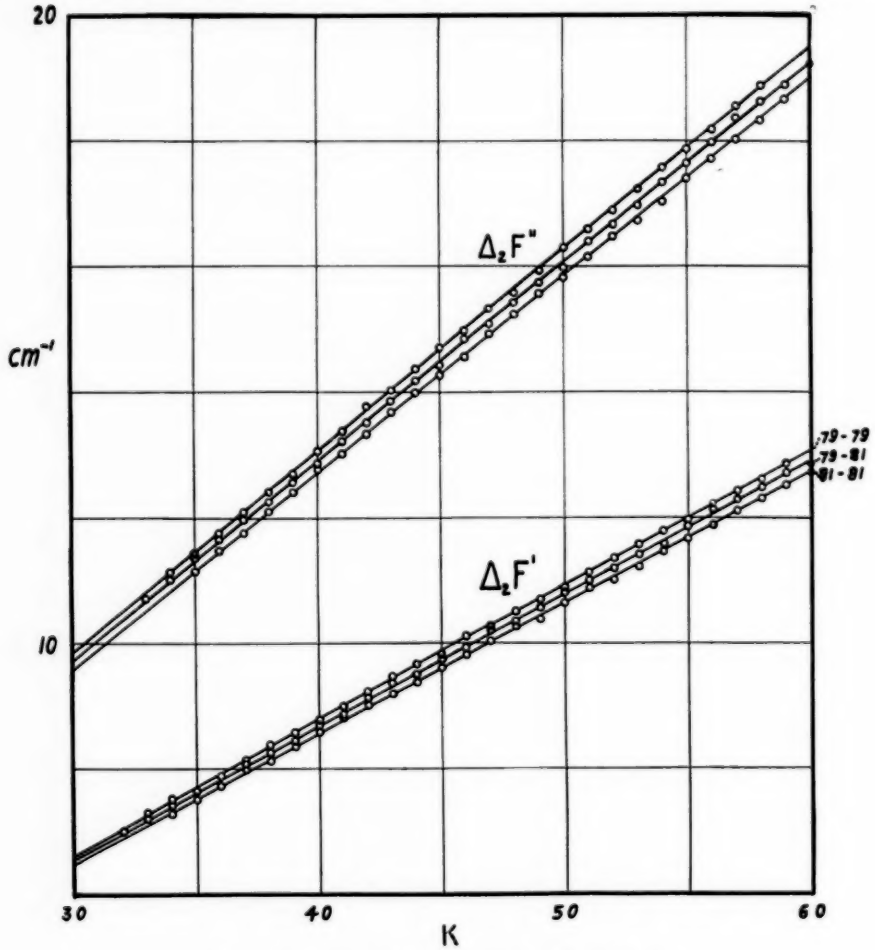

Fig. 2. Combination differences for the 9,4 band.

Br_2^{79} or Br_2^{81} origin relative to that of $Br_2^{79,81}$. In this case terms involving $(v+\frac{1}{2})^3$ are negligible. Table III gives the vibrational analysis together with the vibrational constants of $Br_2^{79,81}$, and in Table IV the "observed" vibrational isotope shifts of Br_2^{79} and Br_2^{81}, and the values of $\delta\nu^\circ$ calculated from equation (6) are given. The agreement is well within the limit of error of the constants used and confirms the vibrational numbering. This is also shown by Fig. 4 where the quantity $\Delta v(\Delta v = \delta G'/\omega_v)$ is plotted against $(v'+\frac{1}{2})$ (cf. Fig. 1 reference 4).

An alternative method of calculating the vibrational isotope shift from the band lines is to consider the separation of corresponding lines as the sum of the vibrational isotope shift, $\delta\nu^{\circ}$, and a rotational shift given by

$$\delta\nu_{\text{rot}} = -({}^{i}B' - B' + {}^{i}B'' - B'')J'' + ({}^{i}B' - B' - {}^{i}B'' + B'')J''^{2}$$

for P lines, and

$$\delta\nu_{\text{rot}} = ({}^{i}B' - B' + {}^{i}B'' - B'')(J'' + 1) + ({}^{i}B' - B' - {}^{i}B'' + B'')(J'' + 1)^{2}$$

for R lines.

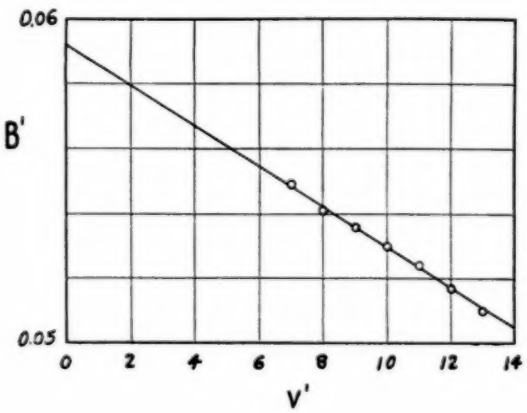

Fig. 3.

TABLE II. *Combination differences for Br_2^{79} and Br_2^{81}.*

	9,4				10,2				11,3			
	Δ_2F''		Δ_2F'		Δ_2F''		Δ_2F'		Δ_2F''		Δ_2F'	
J	79–79	81–81	79–79	81–81	79–79	81–81	79–79	81–81	79–79	81–81	79–79	81–81
33			7.30							10.58		6.97
34	11.15		7.51	7.28			7.34	7.16		10.92		7.08
35	11.42	11.15	7.68	7.50	11.49	11.26	7.57	7.42		11.17		7.33
36	11.76	11.49	7.87	7.72	11.82	11.56	7.83	7.62	11.81	11.50		7.55
37	12.09	11.76	8.14	7.98	12.29	11.91	8.02	7.84	12.13	11.84	7.95	7.81
38	12.41	12.10	8.36	8.12	12.48	12.20	8.38	8.13	12.50	12.19	8.15	7.99
39	12.71	12.41	8.57	8.35	12.92	12.53	8.47	8.28	12.76	12.54	8.37	8.10
40	13.06	12.77	8.77	8.58	13.18	12.84	8.72	8.46	13.07	12.72	8.54	8.33
41	13.38	13.04	8.98	8.81			8.86	8.66	13.45	13.01	8.77	8.53
42	13.68	13.34	9.22	9.00					13.71	13.41	9.00	8.78
43	14.04	13.68	9.47	9.19					14.03	13.72	9.14	8.93
44	14.38	14.00	9.66	9.38								
45	14.71	14.28	9.84	9.61								
46	14.98	14.58	10.11	9.83								
47	15.32	14.94	10.27	10.04								
48	15.59	15.23	10.51	10.26								
49	15.94	15.56	10.71	10.39								
50	16.30	15.81	10.89	10.65								
51	16.58	16.14	11.14	10.89								
52	16.89	16.49	11.36	11.02								
53	17.23	16.73	11.59	11.23								
54	17.57	17.03	11.80	11.47								
55	17.86	17.41	11.99	11.66								
56	18.19	17.72	12.23	11.90								
57	18.56	18.03	12.44	12.11								
58	18.87	18.33	12.63	12.32								
59		18.66	12.88	12.52								
60				12.74								
B obs.	0.08067	0.07855	0.05432	0.05291	0.08129	0.07934	0.05354	0.05238	0.08085	0.07896	0.05298	0.05179
B calc.	0.08066	0.07869	0.05426	0.05299	0.08122	0.07923	0.05362	0.05238	0.08094	0.07896	0.05298	0.05177

TABLE III. *Vibrational analysis of $Br_2^{79,81}$ band origins.*

v' \ v''	2		3		4
7			15,938.36		
			139.11		
8	16,394.24	*316.77*	16,077.47		
	135.26		*135.26*		
9	16,529.50	*316.77*	16,212.73	*314.66*	15,898.07
	131.49		*131.45*		*131.49*
10	16,660.99	*316.81*	16,344.18	*314.62*	16,029.56
			127.64		*127.65*
11			16,471.82	*314.61*	16,157.21
			123.77		
12			16,595.59		
			119.98		
13			16,715.57		

$$\nu = 15{,}891.3 + 169.71\,(v'+\tfrac{1}{2}) - 1.913\,(v'+\tfrac{1}{2})^2 - 323.2\,(v''+\tfrac{1}{2}) + 1.07(v+\tfrac{1}{2})^2$$

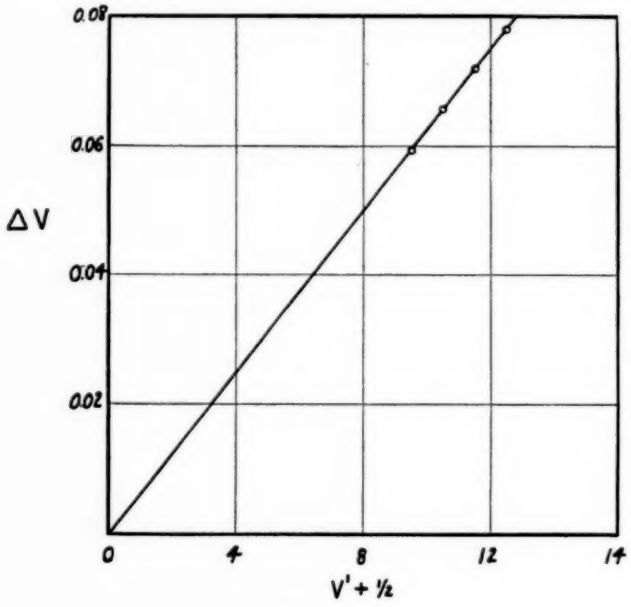

Fig. 4.

TABLE IV. *Observed and calculated vibrational isotope shifts.*

Band	Mol.	Origin	$\delta\nu^\circ$ Obs.	$\delta\nu^\circ$ Calc.
	79–79	16,664.51	+3.52	+3.52
10,2	79–81	660.99		
	81–81	657.43	−3.56	−3.56
	79–79	16,473.97	+2.15	+2.10
11,3	79–81	471.82		
	81–81	469.68	−2.14	−2.16
	79–79	15,897.17	−0.90	−0.90
9,4	79–81	898.07		
	81–81	898.97	+0.90	+0.90
	79–79	16,598.20	+2.61	+2.59
12,3	79–81	595.59		

The difference in D values for the two molecules is negligible. Values of $\delta\nu^0$ calculated in this way for each observed line in the *9,4* band are given in Table V. For some reason the R branch of $Br_2^{79,79}$ gives a value slightly low but the other values are in extremely good agreement with theory.

Alternating Intensities

One of the most interesting questions in connection with the spectrum of bromine is that of the nuclear spins and its effect on the intensities of lines in bands of the symmetrical molecules. Unfortunately this question cannot be answered at present any more than to state that the phenomenon of alternating intensities is definitely observable. This is shown by the intensities given in Table V which are peak height in mm on the microphotometer trace of the *9,4* band reproduced in Fig. 1, the lines originating on odd numbered levels (odd J'') being stronger. Thus the complete wave-function ψ must be antisymmetric in the nuclei, and, like Cl, the Br nuclei obey the Fermi-Dirac statistics in accordance with the usual rule for atoms containing odd numbers of protons. In many respects this is the simplest region of the spectrum yet

Table V. *Lines and isotope shifts in the 9,4 band, P branches.*

J''	Int.	*81,81*	Int.	*79,81*	Int.	*79,79*	$\delta\nu$	$\delta\nu^0$	$\delta\nu$	$\delta\nu^0$
29				15872.24		15871.00			1.24	0.90
30		15871.83	30	870.56	12	869.30	1.27	0.91	1.26	0.90
31	20	870.09	29	868.83	27	867.51	1.26	0.87	1.32	0.93
32	14	868.36	24	867.09	16	865.75	1.27	0.86	1.34	0.93
33	18	866.59	21	865.23	14	863.90	1.36	0.92	1.33	0.89
34	15	864.74	27	863.37	16	861.98	1.37	0.91	1.39	0.93
35	13	862.82	20	861.42	18	860.06	1.40	0.91	1.36	0.87
36	17	860.87	21	859.42	21	858.07	1.45	0.94	1.35	0.84
37	18	858.83	29	857.41	30	855.98	1.42	0.88	1.43	0.89
38	10	856.83	20	855.34	16	853.85	1.49	0.92	1.49	0.92
39	23	854.71	25	853.22	27	851.71	1.49	0.89	1.51	0.91
40	7	852.54	21	851.01	13	849.50	1.53	0.90	1.51	0.88
41	19	850.29	27	848.78	19	847.22	1.51	0.85	1.56	0.90
42	9	848.08	23	846.47	17	844.89	1.61	0.92	1.58	0.89
43	22	845.76	28	844.12	23	842.52	1.64	0.92	1.60	0.88
44	17	843.40	28	841.73	17	840.07	1.67	0.92	1.66	0.91
45	19	840.95	32	839.28	23	837.61	1.68	0.90	1.67	0.88
46	24	838.50	25	836.79	18	835.02	1.71	0.89	1.77	0.95
47	19	835.98	28	834.18	19	832.47	1.80	0.95	1.71	0.86
48	20	833.39	24	831.63	15	829.81	1.76	0.87	1.82	0.93
49	14	830.79	22	828.95	16	827.15	1.84	0.92	1.80	0.88
50	14	828.09	24	826.25	19	824.38	1.84	0.88	1.87	0.91
51	15	825.37	25	823.45	25	821.56	1.92	0.92	1.89	0.89
52	14	822.60	14	820.66	,9	818.71	1.94	0.90	1.95	0.91
53	20	819.77	20	817.80	20	815.81	1.97	0.89	1.99	0.91
54	8	816.89	22	814.90	20	812.84	1.99	0.88	2.06	0.94
55	19	813.97	19	811.88	14	809.83	2.09	0.94	2.05	0.89
56		810.92		808.86		806.78	2.06	0.86	2.08	0.88
57		807.91		805.76		803.63	2.15	0.91	2.13	0.89
58		804.82		802.61		800.45	2.21	0.93	2.16	0.88
59		801.69		799.42		797.20	2.27	0.95	2.22	0.90
60		798.48		796.22			2.26	0.89		
61				792.91						
						Mean		0.903		0.899—
						Theoretical		0.896		0.902—

TABLE V. (*Continued. R branches*).

J	Int.	*81,81*	Int.	*79,81*	Int.	*79,79*	$\delta\nu$	$\delta\nu^0$	$\delta\nu$	$\delta\nu^0$
32				15874.08						
33				872.44		15871.20			1.24	0.88
34		15872.02	27	870.78	10	869.49	1.24	0.86	1.29	0.91
35	27	870.32	28	869.07	24	867.74	1.25	0.84	1.33	0.92
36	19	868.59	28	867.31	19	865.94	1.28	0.85	1.37	0.94
37	19	866.81	21	865.48	15	864.12	1.33	0.88	1.36	0.90
38	20	864.95	26	863.59	14	862.21	1.36	0.88	1.38	0.90
39	24	863.06	26	861.66	24	860.28	1.40	0.89	1.38	0.87
40	8	861.12	16	859.70	16	858.27	1.42	0.88	1.43	0.89
41	16	859.10	29	857.64	23	856.20	1.46	0.90	1.44	0.87
42	9	857.08	25	855.59	12	854.11	1.49	0.90	1.48	0.89
43	23	854.95	31	853.48	24	851.99	1.47	0.85	1.49	0.87
44	12	852.78	27	851.24	13	849.73	1.54	0.89	1.51	0.86
45	23	850.56	33	849.03	21	847.45	1.53	0.85	1.58	0.90
46	13	848.33	24	846.72	11	845.13	1.61	0.90	1.59	0.88
47	25	846.02	27	844.38	25	842.74	1.64	0.90	1.64	0.89
48	15	843.65	26	841.98	13	840.32	1.67	0.89	1.66	0.88
49	25	841.18	26	839.51	19	837.86	1.67	0.86	1.65	0.84
50	17	838.74	23	837.06	17	835.27	1.68	0.83	1.79	0.94
51	23	836.26	28	834.46	23	832.70	1.80	0.91	1.76	0.88
52	19	833.62	29	831.87	19	830.07	1.75	0.83	1.80	0.88
53	14	831.00	23	829.21	19	827.40	1.79	0.84	1.81	0.86
54	14	828.36	25	826.50	16	824.64	1.86	0.87	1.86	0.87
55	12	825.63	18	823.75	20	821.82	1.88	0.85	1.93	0.90
56	16	822.85	21	820.98	9	819.01	1.87	0.80	1.97	0.90
57	24	819.99	25	818.06	22	816.07	1.93	0.82	1.99	0.88
58	5	817.14	19	815.10	17	813.08	2.04	0.89	2.02	0.87
59	17	814.21	18	812.15	12	810.08	2.06	0.87	2.07	0.88
60		811.22		809.10		806.98	2.12	0.89	2.12	0.89
61		808.18		806.04		803.90	2.14	0.87	2.14	0.87
62		805.09		802.88		800.66	2.21	0.90	2.22	0.90
63		801.96		799.70		797.44	2.26	0.90	2.26	0.90
64				796.46						
65				793.17						
						Mean	0.870		0.889	
						Theoretical	0.896		0.902	

TABLE VI. *Rotational constants of bromine.*

	Upper State			Lower State			
	79–79	*79–81*	*81–81*	*79–79*	*79–81*	*81–81*	
B_e	0.0603	0.0595	0.05882	0.08192	0.08091	0.07990	
B_0	0.0600	0.0592	0.05851	0.08178	0.08077	0.07976	
I_e	459	465	471	337.9	342.1	346.4	$\times 10^{-40}$
I_0	461	467	473	338.5	342.7	347.0	$\times 10^{-40}$
r_e	2.65	2.65	2.65	2.28	2.28	2.28	$\times 10^{-8}$
r_0	2.66	2.66	2.66	2.28	2.28	2.28	$\times 10^{-8}$
D_e	3.0	2.9	2.8	2.0	2.0	2.0	$\times 10^{-8}$
α	0.00064	0.000625	0.00061	0.00028	0.000275	0.00027	

the overlapping by the *11,5* and *7,3* bands is a serious complication. It is of interest to note that the nuclear spin $I=3/2$ as deduced from hyperfine structure[9] would result in a ratio of intensities 1.67:1. This value is favored by the present rough measurements but the value $I=5/2$ with a ratio of intensities 1.4:1 is not precluded. This problem requires further study.

[9] DeBruin, Nature **125**, 414 (1930); S. Tolansky, Nature **127**, 855 (1931).

Summary of Constants

Values of the rotational constants are given for the three molecules in Table VI. These form an inter-connecting set as the values for the less abundant molecules were calculated from those for $Br_2^{79,81}$ by means of the various relations given above.

My thanks are due to Professor R. S. Mulliken for suggestions and advice and to Professor G. S. Monk for his cooperation in obtaining best results from the grating.

THE NEAR INFRARED ABSORPTION SPECTRA OF SOME HALOGEN DERIVATIVES OF METHANE

By John G. Moorhead
Northwestern University and Westminster College

(Received January 21, 1932)

Abstract

The infrared absorption spectra of CH_3Cl, CH_3Br, and CH_3I, in vapor form, were measured from 1.5μ to 3.0μ. The fine structure of bands in the 2.3μ region was resolved in the first order. The fine structure of bands in the 1.6μ region was resolved in the second order, but not in the first. Seven bands were found.

Introduction

Bennett and Meyer[1] investigated the infrared absorption spectra of the four halogen derivatives of methane, CH_3F, CH_3Cl, CH_3Br, and CH_3I, in the vapor form. They applied the theory of the spinning top type

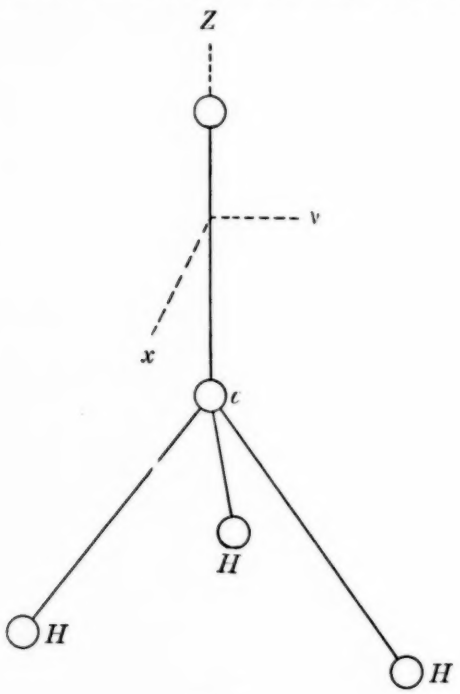

Fig. 1.

of molecule, as developed by Dennison and others.[2] Only a brief outline of the theory is given here. The halogen and the carbon atoms form the only axis of symmetry (see Figure 1). C represents the moment of inertia about Z, the

[1] Bennett and Meyer, Phys. Rev. **32**, 888 (1928).

[2] Dennison, Phys. Rev. **28**, 318 (1926). Other references are given in the article by Bennett and Meyer.

axis of symmetry. A and B represent the moments of inertia about the X- and Y-axes, respectively; then $A = B$. There are two possible normal modes of vibration. In the first type, the change of electric moment vibrates parallel to the axis of symmetry, giving rise to a "parallel" band. In the second type, the change of electric moment vibrates perpendicular to the axis of symmetry, giving rise to a "perpendicular" band.

In this investigation, the spectra of CH_3Cl, CH_3Br, and CH_3I, in vapor form, were studied in the region from 1.5μ to 3μ. Strong bands were found at the 1.6μ and 2.3μ regions. The fine structure of the 1.6μ region was resolved in the second order but not in the first. The fine structure of the bands of the 2.3μ region was resolved in the first order spectra. The bands in these two regions bear much resemblance to those reported by Bennett and Meyer, and the general method used by them in classifying their bands was used in this work.

Experimental Procedure

The apparatus used and procedure followed have been described in a previous paper.[3] The pressures of the gases in the absorption cell are 70 cm Hg for CH_3Cl, 5 cm for CH_3Br and 20 cm for CH_3I. Chemically pure methyl iodide and methyl chloride were furnished by the Eastman Kodak Company. The methyl chloride was furnished by the Matheson Company of North Bergen, N.J. Comparison of the spectra obtained with the possible impurities named in the previous paper showed that the bands were due to the compounds themselves.

Results

Bennet and Meyer[1] found seven series of bands between 3.3μ and 15μ. They classified them, according to their theory, as parallel and perpendicular bands, and lettered them from A to G. These seven series appeared to converge to the methane bands at 7.7μ, 3.3μ, and to the hypothetical methane band at 6.6μ of Dennison's theory,[4] in going from compound to compound of halogens of decreasing atomic weight. Variations were found in the frequency intervals of the Q branches in the perpendicular bands in going from series to series which indicated perturbations between the rotation and vibration. However, the doublet separation, the frequency difference between the maxima of the P and R branches remained quite constant for the same compounds, in going from series to series. No explanation was given for this phenomenon.

In this investigation seven bands were found in the region from 1.5μ to 2.5μ. These were lettered from H to N.

The Individual Series

H Series. Parallel Type. The frequencies of the maxima of the P and R branches, and the doublet spacing, that is, the spacing of these maxima, are shown in Table VIII. These bands are not shown in the diagrams. The H band is a deep double band in all three compounds. The wave-lengths de-

[3] Moorhead, Phys. Rev. **39**, 83 (1932).

[4] Dennison, Astrophys. Jour. **62**, 84 (1925).

crease rapidly with decreasing atomic weight of the halogen atom and the bands appear to converge to one of the methane bands in the 2.31μ region. Accurate readings were difficult because of a region of atmospheric water vapor bands.

I and J Series. Perpendicular Type. The wave-lengths of the lines of these bands are given in Tables I, III, and V. The curves are shown in Fig. 2. These

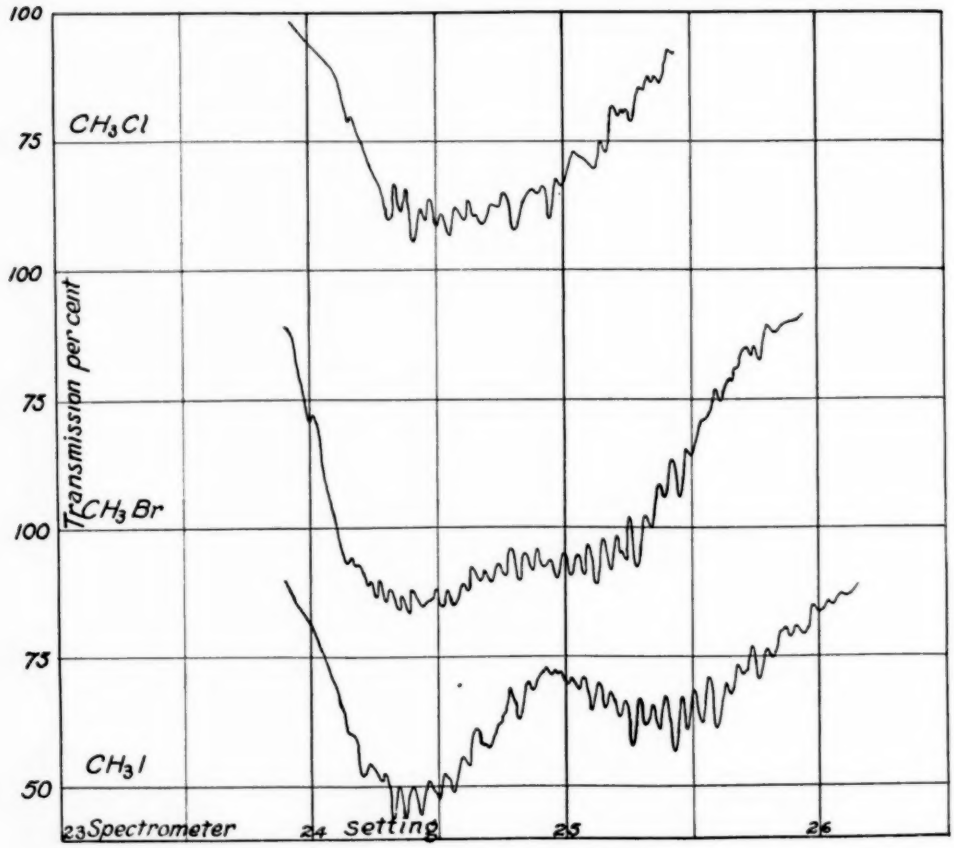

Fig. 2. Left *J*-Band. Right *I*-Band.

bands are clearly separated in the iodide, but converge more and more closely toward each other in passing to halides of smaller atomic weight. In this convergence, the wave-lengths of the *I* band decrease, while those of the *J* band increase. These bands converge to one or two of the methane bands in the 2.2 μ region. Part of the fine structure is very uniform and distinct in the iodide and bromide, but in the chloride it is confused because of the overlapping of the two bands. In parts of the iodide and bromide bands, every third line is deeper than the other two. This characteristic was noted by Bennett and Meyer in some of the bands investigated by them. No simple explanation of this appears possible. In all the compounds the *J* band appears to be stronger than the *I* band.

K and L Series. Parallel Type. M Series. Perpendicular Type. The wave-lengths of the lines are given in Tables II, IV, and VI. The maxima of the envelopes and doublet spacing of the parallel bands are shown in Table VIII. The frequency differences of the Q branches of the M band are shown in Table IX. Fig. 3. shows the second order spectra of these bands. These three series form a deep band region. The intensities, wave-lengths, and general appearance of the bands are similar for all three compounds, and they also bear

TABLE I. *Methyl chloride 2.3μ band region.*

Spectrometer Setting	Wave-Length μ	Frequency cm^{-1}	Spectrometer Setting	Wave-Length μ	Frequency cm^{-1}
24.31	2.2212	4502.0	25.12	2.2936	4360.0
.36	2.2253	4493.8	.17	2.2983	4351.0
.41	2.2297	4484.9	.215	2.3022	4343.6
24.455	2.2337	4476.9	.235	2.3040	4340.3
.505	2.2382	4467.8	.27	2.3070	4334.6
.555	2.2427	4458.9	.325	2.3120	4325.3
.61	2.2478	4448.8	.35	2.3142	4321.1
.66	2.2522	4440.1	.385	2.3175	4315.0
.68	2.2541	4436.4	.445	2.3230	4304.8
.745	2.2600	4424.8	.555	2.3330	4286.3
.81	2.2658	4413.5	25.585	2.3356	4281.6
.90	2.2740	4397.5	.67	2.3432	4267.6
.945	2.2782	4389.4	26.685	2.4340	4108.5
.995	2.2827	4380.8	.905	2.4537	4075.6
			27.035	2.4653	4056.2
			27.16	2.4768	4037.5

TABLE II. *Methyl chloride 1.6μ band region, second order.*

Spectrometer Setting	Wave-Length μ	Frequency cm^{-1}	Frequency Difference cm^{-1}	Spectrometer Setting	Wave-Length μ	Frequency cm^{-1}
35.89	1.6248	6154.6	10.2	37.12	1.6785	5958
.95	1.6275	6144.4	11.	.23	1.6834	5940
36.01	1.6304	6133.4	9.6	.30	1.6865	5930
.07	1.6329	6123.8	13.2	.34	1.6882	5924
.15	1.6365	6110.6	9.8	.44	1.6926	5908
.21	1.6391	6100.8	15.4	.54	1.6969	5893
.305	1.6432	6085.4	10.4	.62	1.7004	5881
.37	1.6461	6075.0	12.8	.68	1.7030	5872
.45	1.6495	6062.2		.78	1.7074	5857
.62	1.6565	6037.		.90	1.7127	5839
.84	1.6661	6002.		38.06	1.7197	5815
.97	1.6721	5980.		.18	1.7249	5797
				.26	1.7285	5785

much resemblance to the E, F, and G group of bands described by Bennett and Meyer. The K and L series are parallel bands superposed on the wise absorption region which is supposed to be a single series, Series M. In the case of the iodide, the K band appears to have P and R branches but no Q branch. In the bromide and chloride, the K bands appear to have P, Q, and R branches, although they are so masked by the fine structure of the M series that the maxima of the envelopes cannot be determined. In each of the compounds, the L series stands out prominently from the background of the M

TABLE III. *Methyl bromide 2.3μ band region.*

Spectrometer setting	Wavelength μ	Frequency cm^{-1}	Frequency difference cm^{-1}	Spectrometer setting	Wavelength μ	Frequency cm^{-1}	Frequency difference cm^{-1}
24.00	2.1930	4560.0		25.12	2.2937	4359.8	10.3
.145	2.2060	4533.1		.18	2.2991	4349.5	10.1
.16	2.2072	4530.6		.24	2.3045	4339.4	
.22	2.2127	4519.3	6.3	24.285	2.3083	4332.2	7.2
.255	2.2158	4513.0	7.5	.34	2.3134	4322.6	9.6
.295	2.2195	4505.5	8.1	.39	2.3180	4314.1	8.5
.34	2.2235	4497.4	8.1	.45	2.3233	4304.2	9.9
.385	2.2275	4489.3	10.6	.50	2.3280	4295.5	
24.445	2.2328	4478.7		.615	2.3383	4276.6	
.515	2.2392	4465.9		.72	2.3478	4259.3	
.56	2.2432	4457.9		.825	2.3570	4242.7	
.61	2.2477	4449.0		.97	2.3702	4219.0	
.66	2.2522	4440.1		26.10	2.3818	4198.6	
.705	2.2563	4432.0		.23	2.3935	4178.0	
.765	2.2618	4421.3		.33	2.4025	4162.3	
.82	2.2666	4411.9	9.2	.42	2.4105	4148.5	
.87	2.2713	4402.7	7.7	.49	2.4167	4138.0	
.915	2.2753	4395.0	8.4	27.30	2.4894	4017.0	
.965	2.2797	4386.6	9.8	27.46	2.5046	3992.8	
25.02	2.2848	4376.8	9.2	27.85	2.5384	3939.5	
.075	2.2896	4367.6	7.8	28.20	2.5697	3891.5	

TABLE IV. *Methyl bromide 1.6μ band, second order.*

Spectrometer setting	Wavelength μ	Frequency cm^{-1}	Frequency difference cm^{-1}	Spectrometer setting	Wavelength μ	Frequency cm^{-1}	Frequency difference cm^{-1}
35.985	1.6291	6138.2		37.10	1.6777	5960.4	9.2
36.05	1.6320	6127.4		.16	1.6803	5951.2	9.4
.10	1.6343	6118.8		.22	1.6830	5941.8	10.
.185	1.6380	6105.0		.285	1.6858	5931.8	
.255	1.6410	6093.8		.47	1.6939	5903.	
.45	1.6496	6062.0		.56	1.6978	5890.	
.595	1.6559	6039.0		.65	1.7018	5876.	
36.965	1.6720	5980.8	11.4	.76	1.7065	5860.	
37.04	1.6752	5969.4	9.0	37.84	1.7102	5847.	

TABLE V. *Methyl iodide 2.3μ band.*

Spectrometer setting	Wavelength μ	Frequency cm^{-1}	Frequency difference cm^{-1}	Spectrometer setting	Wavelength μ	Frequency cm^{-1}	Frequency difference cm^{-1}
24.20	2.2108	4523.2		25.21	2.3017	4344.6	8.5
.27	2.2172	4510.2	8.9	.26	2.3062	4336.1	9.
.32	2.2216	4501.3	9.3	.31	2.3110	4327.1	9.7
.37	2.2262	4492.0	10.7	.365	2.3162	4317.4	9.9
.43	2.2315	4481.3	12.6	.43	2.3215	4307.5	8.5
.50	2.2378	4468.7	10.	.48	2.3261	4299.0	9.9
.555	2.2428	4458.7		.54	2.3315	4289.1	8.3
.63	2.2497	4444.5		25.59	2.3360	4280.8	10.1
.66	2.2522	4440.1		.65	2.3415	4270.7	8.7
.70	2.2558	4433.0		.705	2.3463	4262.0	9.1
.81	2.2658	4413.5		.76	2.3513	4252.9	8.8
.87	2.2712	4402.9		.815	2.3562	4244.1	
.94	2.2775	4390.8		.89	2.3632	4231.5	
25.005	2.2832	4379.8	7.8	.94	2.3675	4223.9	
.05	2.2873	4372.0	9.	26.01	2.3740	4212.3	
.10	2.2920	4363.0	8.9	.055	2.3778	4205.6	
.155	2.2967	4354.1	9.5	27.78	2.5322	3949.0	
				27.95	2.5475	3925.4	

series, exhibiting P and R branches and the very definite absence of a Q branch. The M series is a wide region of absorption. The band centers could not be determined, due to the presence of the K and L bands. Where sections

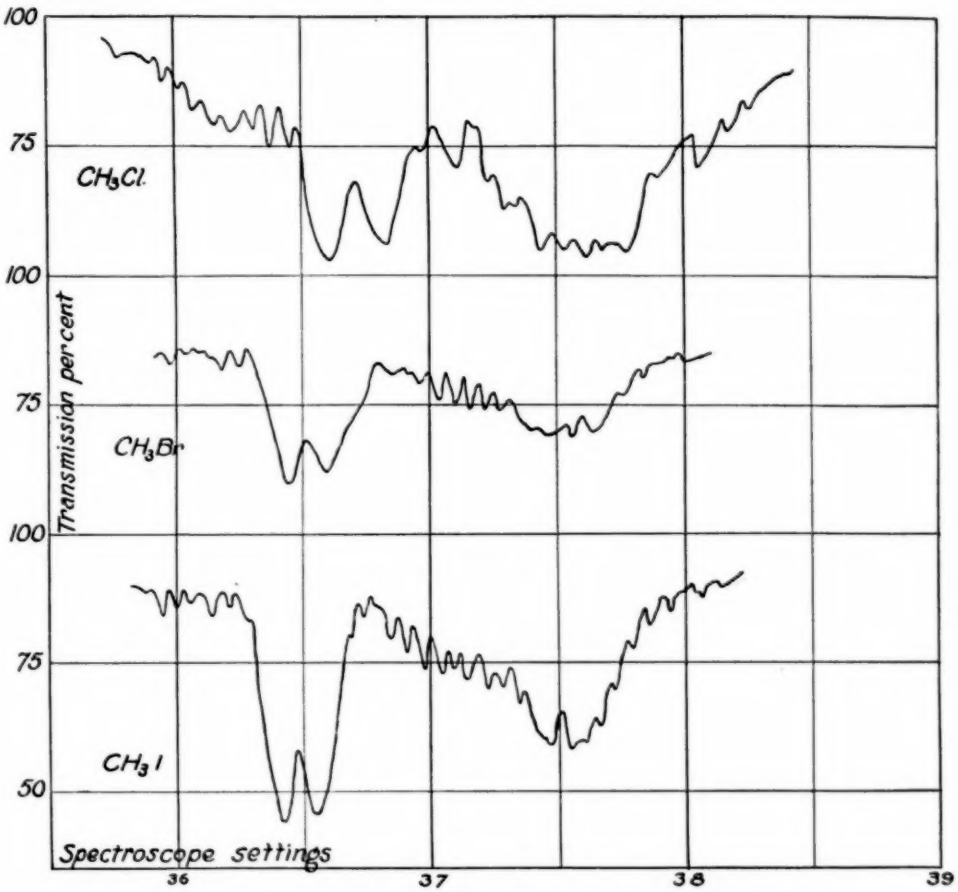

Fig. 3. Left L-Band. Right K-Band. M-Band as background.

TABLE VI. *Methyl iodide 1.6μ band, second order.*

Spectrometer setting	Wave-length μ	Frequency cm^{-1}	Frequency difference cm^{-1}	Spectrometer setting	Wave-length μ	Frequency cm^{-1}	Frequency difference cm^{-1}
35.95	1.6275	6144.2	9.8	37.095	1.6775	5961.2	7.6
36.005	1.6301	6134.4	9.2	.145	1.6796	5953.6	12.6
.06	1.6326	6125.2	14.6	.225	1.6832	5941.0	9.2
.15	1.6365	6110.6	9.8	.285	1.6858	5931.8	9.8
.21	1.6391	6100.8	12.2	.35	1.6886	5922.0	
.285	1.6424	6088.6		.46	1.6934	5905.	
.42	1.6482	6067.0		.55	1.6973	5892.	
.55	1.6539	6046.4		.61	1.7000	5882.	
.74	1.6621	6016.2		.66	1.7021	5875.	
.84	1.6665	6000.6	10.8	.72	1.7048	5865.	
.91	1.6695	5989.8	10.	.79	1.7079	5855.	
.975	1.6724	5979.8	11.	.86	1.7110	5845.	
37.045	1.6753	5968.8	7.6	.94	1.7145	5833.	

of sufficient regularity could be picked out, the frequency differences of the Q branches were computed.

TABLE VII. *Band centers 1.6μ region, first order.*

Spectrometer Setting	Wave-Length μ	Frequency cm^{-1}	Series
	Methyl Chloride		
15.80	1.4500	6896.	*N*
18.09	1.6582	6031.	*L*
18.19	1.6673	5998.	
18.55	1.7000	5882.	*K*
	Methyl Bromide		
15.85	1.4543	6876.	*N*
18.00	1.6500	6061.	*L*
18.08	1.6572	6034.	
18.52	1.6970	5893.	*K*
	Methyl Iodide		
16.03	1.4706	6806.	*N*
17.97	1.6472	6071.	*L*
18.05	1.6545	6044.	
18.55	1.7000	5882.	*K*

TABLE VIII. *Maxima of the envelopes of the branches, parallel bands. Observed frequencies.*

Series	*P* Branch	*R* Branch	Doublet Spacing
	Series *H*		
CH_3Cl	4037. cm^{-1}	4065. cm^{-1}	28 cm^{-1}
CH_3Br	3993.	4017.	24
CH_3I	3925.	3949.	24
	Series *K* (second order) Approximate centers		
CH_3Cl		5880. cm^{-1}	
CH_3Br		5890.	
CH_3I		5900.	
	Series *L* (second order)		
CH_3Cl	6002. cm^{-1}	6037. cm^{-1}	35 cm^{-1}
CH_3Br	6036.	6062.	26
CH_3I	6046.	6067.	21
	First order		
CH_3Cl	5998.	6031.	33
CH_3Br	6034.	6061.	25
CH_3I	6044.	6071. (App)	27 (App)

	Doublet Spacing (Bennett and Meyer)			
Series	CH_3F	CH_3Cl	CH_3Br	CH_3I
A	43 cm^{-1}	35 cm^{-1}	cm^{-1}	cm^{-1}
C	—	28	25	23
E	44	23	23	21
F	—	28	23	21

N Series. This band was found to be very weak in all the compounds studied. Repeated observations were taken and the band was proved to be genuine, but nothing could be learned about its type. This band probably converges to the 1.37μ band of methane. No curves are shown of this band.

Comparison Between the Series

Table VIII gives the doublet separation of the parallel bands measured by the author, and also the doublet separations of the bands measured by Bennett and Meyer. This doublet separation remains nearly constant with the same compound for different series. Part of the variation is due to the errors of observation. The doublet spacing in general increased with the decrease in atomic weight of the halogen in the compound. The doublet spacings of the bands studied in this investigation agree well with the results given by Bennett and Meyer.

Table IX shows the frequency difference for the bands in the different perpendicular series. In most cases, only short sections were available so that the accuracy possible is not high. With this limitation in mind, it is seen that the frequency difference of the three bands measured does not vary much

Table IX. *Average frequency intervals between lines perpendicular type (methyl halides).*

	Moorhead			Bennett and Meyer		
	Series *I* cm^{-1}	Series *J* cm^{-1}	Series *M* cm^{-1}	Series *B* cm^{-1}	Series *D* cm^{-1}	Series *G* cm^{-1}
CH_3F	—	—	—	5.65	11.5	7.5
CH_3Cl	—	—	11.55	6.95	12.	8.2
CH_3Br	9.0	8.1	9.8	7.42	11.9	9.0
CH_3I	9.5	10.3	10.3	7.70	11.8	9.0

from band to band, or from compound to compound in the same band. According to the simple theory, the frequency difference depends upon the moment of inertia, C, and this should be the same for all compounds in the same series, unless there is a finite displacement of the hydrogen atoms in the molecule. It is seen in Table IX that this variation of the frequency differences is greater in the series investigated by Bennett and Meyer than in the series investigated by the author.

I am indebted to the Department of Physics of Northwestern University for the facilities to carry on this work and to Professor B. J. Spence under whose direction the work was performed.

ABSORPTION AND RESONANCE OF THE HELIUM INFRARED LINES

By M. R. Wehr
Randal Morgan Laboratory of Physics, University of Pennsylvania

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Abstract

The absorption of helium excited at low voltages for its own lines, the 2^3S-2^3P at 10830A and the 2^1S-2^1P at 20582A, is determined. The percentage absorption of the 2^3S-2^3P line increases when either the exciting current or the pressure in the absorbing tube is increased, and also when either the current or the pressure in the source tube is decreased. When the light to be absorbed is taken end on from a Geissler tube source, the percentage absorption is much less than when the light is taken off at right angles to the capillary. The changes with source tube conditions are ascribed to the corresponding variations of the shape and width of the emission line. Observable absorption begins when the exciting voltage is 25 volts. No absorption is detected at 19.8 volts, the excitation potential of the 2^3S state. The 10830A line shows strong resonance which is directly proportional to the percentage absorption. The absorption for the 20582A line is very small. It shows no detectable resonance.

Introduction

THE only radiations which helium atoms in the normal or unexcited state can absorb lie in the far ultraviolet corresponding to the removal of the electron directly from the $1S$ level of the atom. The absorption of unexcited helium[1] for its own radiation has been investigated. The absorption of helium when in the excited state, i.e., after the electron has been lifted from the $1S$ level, has also been studied. The radiations involved here lie in the visible[2,3,4] and infrared[5] regions. In all previous studies of the excited gas, the excitation has been secured by maintaining a high voltage discharge through it at 1000 volts or more.

Critical potential measurements have shown that the helium atom can be put into its first higher energy state by bombardment with electrons which have fallen through a potential difference of 19.77 volts. Specifically, the excitation function[6,7] of the 1^1S–2^3S state of helium shows that at a few tenths of a volt above this critical value, a number of atoms are already in the 2^3S state. In the investigation reported here, the absorption and resonance of helium for its own infrared lines, the 2^3S–2^3P at 10830A and the 2^1S–2^1P at 20582A, is measured while the excitation is maintained by a low voltage discharge. The potentials employed are close to the ionization potential. The infrared lines are particularly suitable for this work because: first, these lines

[1] Weatherby and Wolf, Phys. Rev. **29**, 135 (1927).
[2] McCurdy, Phil. Mag. **2**, 529 (1926).
[3] Takamine and Suga, Phil. Mag. **5**, 141 (1928).
[4] McLennan, Ruedy, and Allin, Proc. Roy. Soc. Can. **22** Sect. **3**, 273 (1928).
[5] Paschen, Ann. d. Physik **45**, 625 (1914).
[6] Dymond, Proc. Roy. Soc. **107**, 291 (1924).
[7] Glockler, Phys. Rev. **33**, 175 (1929).

are by far the strongest in the spectrum; second, they are easily isolated by means of filters, thus avoiding the use of a spectrometer and consequent light loss; and third, previous work shows that they are highly absorbed.

Apparatus

The general arrangement of apparatus is shown in Fig. 1. The absorption tube A is of Pyrex and has plane windows at the ends. The field-free anode is a rectangular nickel box 9.6 cm long and 1.5 cm by 1.5 cm in cross section. Each end face has a slit 0.4 cm wide and 1 cm high in its center. The light to be absorbed passes through these slits lengthwise along the box. The gas inside the anode can be illuminated at right angles to its length through the nickel gauze which forms the one side. The bottom is also of gauze, and is insulated from the box so that the currents to each can be read separately when desired. The oxide-coated, equipotential cathode is a cylinder 11 cm

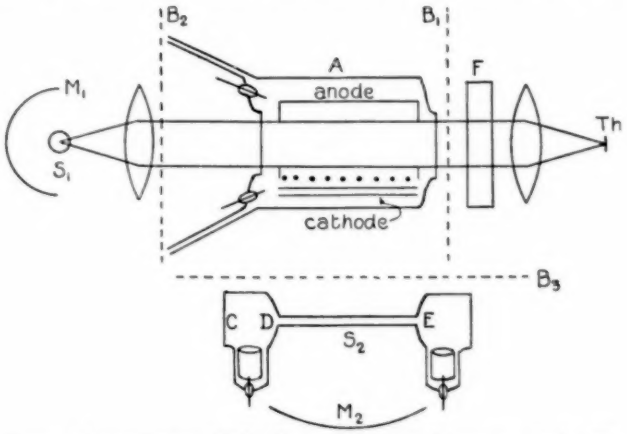

Fig. 1. Arrangement of apparatus. This diagram is not drawn to scale. The source S_2 and mirror M_2 are actually mounted at the same height as the center of the anode.

long, and is made of nickel tubing which has a 1.5 mil wall and is 80 mils in diameter. The cathode is heated internally by a 15 mil tungsten wire contained in a thin walled quartz tube. The coating material is prepared by mixing equal parts by weight of $SrCO_3$ and $BaCO_3$ in a little water. The cathode is 3 mm below the anode. Two strips of mica placed above the cathode and parallel to it, limit practically all of the excitation of the gas within the anode to the region in line with the slits. The tungsten leads are brought in through the stopper which is waxed in one end.

The sources, S_1 for the absorption measurements and S_2 for the resonance measurements, are Pyrex Geissler tubes which have an inside diameter of 3 mm. The capillary of the former is 5.5 cm long, and of the latter, 10 cm. The electrodes are of thin sheet molybdenum. This metal is more satisfactory than aluminum because of the ease with which it can be degassed. S_1 is mounted vertically, and S_2 horizontally. The large concave spherical mirror M_2 images S_2 along the line of the anode slits. The cylindrical mirror M_1 reflects in the direction of the absorbing column the light coming from the

back and sides of S_1, and thus increases the effective source intensity. By putting a mirror in the place of S_1, light taken end on from S_2 can be used for absorption measurements.

Two 350 volt airplane radio generators connected in series drive the sources. In order to have the light from S_1 of sufficiently constant intensity over the period of a reading, it is necessary that the voltage shall not vary by more than 1 part in 10000. Storage batteries floated across the generators maintain the necessary constancy.

The filter[8] for the isolation of the 10830A line consists of two Wratten and Wainwright gelatines, F29 and H45, mounted in *B* glass, and a 1 cm water cell. The filters form the sides of the cell. A sheet of biotite[9,10] 0.19 mm thick serves to isolate the 20582A line. The transmission curves of these filters were obtained with an infrared spectrometer and were found to agree with those given in the reference articles.

In the early stages of the work, an intensity measuring system which consisted of a Thalofide cell placed in one arm of a Wheatstone bridge[11] was employed. This arrangement is highly sensitive to light in the region 1μ. Unfortunately, the resistance changes of the Thalofide cells available for this work were not directly proportional to light intensity and there was no constant relation between these quantities. The cells also had a troublesome time lag.

The measuring instrument used in the final arrangement is a Burt compensated junction, vacuum thermocouple. A Leeds and Northrup *HS* galvanometer which has a resistance of 14 ohms is connected to the thermocouple. The resistance of the thermocouple is 35 ohms which is just slightly higher than the critical external damping resistance of the galvanometer. The actual distance from galvanometer to scale is 525 cm, but the effective distance is made twice as great by allowing the light beam reflected from the galvanometer mirror to fall on a stationary mirror outside the case from which it is reflected back to the galvanometer and from there to the scale. The scale can easily be read to 0.5 mm. A test of the galvanometer response shows that the deflections over the range of the scale, 50 cm, are directly proportional to the e.m.f. applied. The drift due to changes in room temperature is negligible —about 1 mm per hour.

Procedure

The system is evacuated in the usual way. The charcoal traps are heated at 350°C for a number of hours, and the metal parts degassed with an induction heater. When the pressure remains at less than 10^{-5} mm with the heaters on, the pumps are cut off, and the traps immersed in liquid air. About an hour later, helium which has been over charcoal at liquid air temperature, is allowed to flow into the system slowly. The purity of the gas is tested by observing the spectrum in both the source and absorption tubes when run at currents several times higher than the maxima used during observations. In

[8] Paschen, Ann. d. Physik **43**, 858 (1914).
[9] Konigsberger, Ann. d. Physik **61**, 687 (1897).
[10] Ignatieff, Ann. d. Physik **43**, 1117 (1914).
[11] Barnes and Fulweiler, Phys. Rev. **32**, 618 (1928).

order to maintain the purity of the gas, the traps attached to the tubes are kept immersed in liquid air. The cathode is activated by heating, and by bombardment with helium ions.

The method of taking absorption readings is as follows: shutters B_2 and B_3 (Fig. 1) are closed, and B_1 is open; S_1 is running; and the cathode is at working temperature. The galvanometer deflection upon opening B_2 is J_1, the intensity of the source. B_2 is then closed and the gas in A excited by applying a voltage between the cathode and anode. The deflection when B_2 is then opened is J_2, the intensity of the transmitted light. The percentage absorption is $100(J_1-J_2)/J_1$.

The following is the method of taking the resonance readings: B_1 is open and B_2 and B_3 are closed; and the absorption tube and S_2 are operating. The deflection when B_3 is opened is the resonance reading.

Results

The curves in Fig. 2 show the variation of the percentage absorption for the 2^3S-2^3P line when the conditions in S_1 are varied and those in A re-

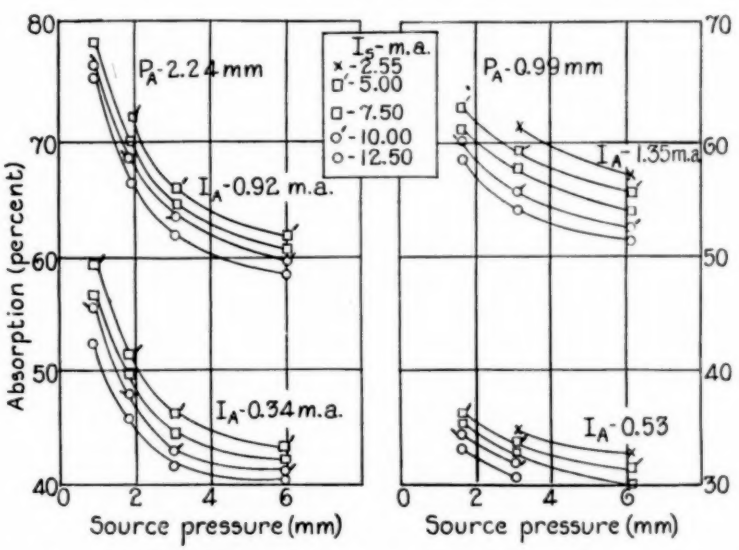

Fig. 2. Absorption 10830A line as a function of source tube conditions. The anode voltage is 29 volts. I_A is the anode box current, P_A the absorption tube pressure, and I_S the current in the source tube (vertical one used).

main fixed. In general, the percentage absorption increases when either the pressure or the current in the source decreases. Similar groups of curves, which are not given here, obtained with other sets of source and absorption tube conditions, show the same effect. It is obvious that if one is to get comparable results for changes in absorbing tube conditions, then the source conditions must remain fixed throughout. The results obtained will depend, of course, on the particular set of fixed conditions chosen for the source.

Fig. 3 depicts the variation of the percentage absorption for the 10830A line when the pressure and current in A are varied. The current to the box

is taken as the abscissa because that current is the one principally responsible for exciting the atoms in the path of the source light. The curves are flatter if the total current is used. The dotted line curve is obtained when the light to be absorbed is taken end on from S_2. This and other curves obtained in the same way show that the absorption is always considerably less then than when light is taken from the vertical capillary of S_1.

The intensity of the 2^1S-2^1P line emitted by the source is so small that absorption measurements can not be made with reasonable accuracy. The indications are, however, that the absorption for this line is small.

The resonance curves for the 10830A line are not shown here. In every case the readings are directly proportional to the percentage absorption, and

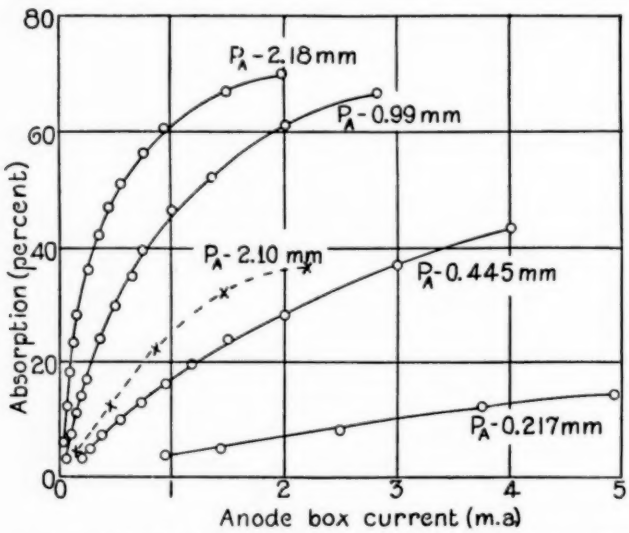

Fig. 3. Absorption of 10830A line as a function of absorption tube conditions. The anode voltage is 29 volts, the source tube current 7.5 milliamperes, and the source tube pressure 6.10 mm. The full line curves are obtained with the vertical capillary source, and the dotted curve with the end on source.

the plot of them can be made to coincide with the corresponding absorption curve by choosing the proper ordinate scale. The largest resonance deflection is 8 cm. The 20582A line shows no resonance.

There is no appreciable variation of absorption with voltage within the range of 25 to 30 volts. The voltage in the range 17 to 22 volts is varied in 0.1 volt steps. If there is any absorption within that range, it is less than 0.1 percent, the smallest detectable amount.

No change of absorption is noticeable when the light from S_1 is polarized and its plane rotated. Such a change might be expected from impact polarization of the atoms in A resulting from collisions with the unidirectional electron stream from the cathode. Some of the desiderata in observing impact polarization are low gas pressures, and at times also, low excitation voltages. To determine polarization under such conditions by the usual methods is difficult because of the low intensities of the emission lines. Absorption measurements with polarized light may be a helpful and more powerful tool in such cases, since then the smallest detectable change will

depend on the intensity of the source and this can be varied at will. The failure to notice any change in absorption in this work may have been caused by insufficient uniformity of the electron stream, and by the presence of an undetermined magnetic field due to the cathode heating current, the earth's field, and nearby iron pipes. This problem of absorption of polarized light will be investigated in the near future with more appropriately designed apparatus.

For fixed conditions in the source and absorption tubes, the percentage absorptions obtained in a series of readings check to within 0.4 percent absorption when the galvanometer deflections range from 10 to 40 cm, which is the case at the higher pressures and currents in S_1. In most cases the elapsed time between the first and check determinations is several days. The errors increase of course as the galvanometer deflections decrease. When the source current is equal to or less than 5 milliamperes and the pressure in S_1 is less than 2 mm, the largest difference between the values obtained with fixed conditions for the percentage absorption is 2 percent absorption.

Interpretation of Results

The low percentage absorption obtained when taking light end on from S_2 can be explained on the basis of the intensity distribution in the emitted line. Some light in the central portion of the line emitted by the atoms in the capillary of S_2, DE, is absorbed by the less strongly excited atoms in the wide portion of the tube, DC. This will not occur in the case of S_1 because the light from it is taken off at right angles to the capillary. Therefore, the line from S_2 will have a larger percentage of its energy in the wings of the frequency-energy distribution curve than will the one from S_1, but conversely for the central portions. The emission line from the absorption tube A is narrower than that from either of the source tubes because both the temperature and pressure are lower. Thus, the fraction of the total light from S_2 which can be absorbed in A is less than that for S_1.

The change in percentage absorption at constant source pressure when the source tube current is varied is due to the resulting temperature change of the excited gas. An increase in current causes a rise in temperature, and therefore, the source line becomes correspondingly broader. The percentage absorption will then decrease because the energy absorbed in A is a smaller fraction of the energy in a wide line than it is of that in a narrow one.

An increase in pressure also causes a broadening of the line. Thus the percentage absorption will also decrease when the current is kept constant and the pressure is increased.

The percentage absorptions represented by the first parts of the curves in Fig. 3 are directly proportional to the anode current I_A. After the percentage absorption has reached a value of 10 percent, the curves are given approximately by the equation $A = S \log I_A + m$. S is a constant which is the same for all the curves, and m, a constant which is different for each. The greatest deviation of this equation from the observed values is about 2 percent absorption. This is somewhat larger than the experimental error.

The author wishes to thank Dr. C. B. Bazzoni for suggesting this problem and for his aid and interest in its solution.

INTENSITY MEASUREMENTS IN THE ARC SPECTRUM OF THALLIUM

By S. E. Williams and J. Herlihy

Department of Physics, Sydney University, Australia

(Received October 28, 1931)

Abstract

Intensity ratios for the doublets of the principal series, $2s-mp_{1\frac{1}{2}}$, $2s-mp_{\frac{1}{2}}$, were measured by the photographic method, using a Pfund arc with silver poles. For $m=4$, 5, 6, 7, the values obtained for $\overline{a_1^2}/\overline{a_2^2}$ were 4.4, 6.6, 6.0, 5.2, deviating substantially from the prediction of the sum rule, and showing the effect discovered by Sambursky in the principal series of the alkalies. Separation of results according to arc currents of 2 amp. and 4 amp. showed no effect due to this factor. For the doublet $m=4$, the ratio obtained with a copper arc was 2.5. The relative intensities of the stronger components $(2s-mp_{1\frac{1}{2}})$, for values of $m=4$, 5, 6, 7, 8, were found to be 850, 82, 17.5, 3.2, and 1, respectively.

THE investigations of intensities in the doublet series of the alkali arc spectra carried out by Sambursky and others have revealed several interesting properties. It was therefore of interest to examine the doublet spectrum of a metal of the third group.

Measurements of the ratios for the principal doublets of the thallium arc spectrum were first made by O. U. Vonwiller,[1] at Utrecht, in 1929, but insufficient data were obtained for comparison with previous work. During 1930 the examination of the principal series was continued in Sydney.

The photographic methods introduced by Ornstein, and developed by him and his co-workers at Utrecht, were employed with very slight modifications, necessitated, in the case of one or two doublets, by the difficulty of obtaining suitable photographs. A Hilger spectrograph, of constant deviation type, was used with Ilford Special Rapid Panchromatic plates, which were found suitable for the whole of the range covered, *viz.*, 6700–4750A. By using the varying slit method, twelve exposures to continuous spectra were made on each plate in order to provide density marks, the source being a tungsten filament lamp previously calibrated by Mr. D. Vermeulen, of the Physical Laboratory, Utrecht University.

Preliminary observations on the second doublet of the series were made with a Pfund arc having copper poles. The presence of copper lines almost coincident with the components of the fourth doublet, (5109–5136A), made other means of producing the spectrum desirable. Attempts to excite the spectrum in an electrically heated discharge tube were unsuccessful owing to the sublimation of the metal on the walls of the tube. In nickel, monel metal, and carbon (cored with the chloride), the lines are so numerous that identification is too difficult to give reasonable certainty that the thallium lines, if

[1] O. U. Vonwiller, Phys. Rev. **35**, 802 (1930).

present, are unobscured by a background due to the material forming the poles. Spectra were finally obtained by using a Pfund arc with silver poles, all desired lines being free of any background.

At the expense of some loss of intensity, the illumination was so arranged that the region of the arc used was variable at will by means of diaphragms, light from each point falling uniformly onto the slit of the spectrograph.

No members of the series beyond the sixth were observed in any photographs and measurements could only be made as far as the fifth member (4891–4906A). For the doublets in the red and yellow exposures of a few seconds were sufficient but with those in the green and blue the intensity is so much less that half an hour is necessary. In such exposures the effect of continuous spectrum was greatly increased but this was found to be of advantage in giv ng more definite corrections for the rough ratios.

The combined results are given in Table I, the ratio given being that of the component of shorter wave-length ($2s-mp_{1\frac{1}{2}}$), to that of longer wave-length, ($2s-mp_{\frac{1}{2}}$). The value $\overline{a_1^2}/\overline{a_2^2}$ is obtained from I_1/I_2 by multiplying by the factor $(\lambda_2/\lambda_1)^4$, a_1, a_2, being the amplitudes of the virtual oscillators given by the equation $I=a^2\nu^4$. It will be seen that there is definite evidence of a maximum ratio occurring at the third member of the series. This is in accord with the observations of Sambursky[2] on the doublet spectra of the alkalies.

TABLE I. *Principal series doublets, $2s-mp_{1\frac{1}{2}}$, $2s-mp_{\frac{1}{2}}$.*

m	Wave-lengths	No. of obs.	Mean (I_1/I_2)	Mean $(\overline{a_1^2}/\overline{a_2^2})$	Average error	Probable* error
4	6549–6713A	7	4.9	4.4	0.8	0.3
		†9	2.8	2.5	0.5	0.2
5	5528–5583A	19	6.9	6.6	1.0	0.25
6	5109–5136A	22	6.1	6.0	1.0	0.2
7	4891–4906A	21	5.25	5.2	0.9	0.2

† Copper arc.
* Probable errors calculated with Peter's approximation formula

$$\text{P.E.}=\frac{0.8453\ \Sigma(+v)}{n(n-1)^{1/2}}.$$

Included in the table is the additional value obtained for the second member by use of an arc having copper poles. The difference between the two values, 4.4 and 2.5, is very much greater than the error considered possible in the mean results and presumably is to be attributed to different conditions (temperature, etc.) in the arc with different poles. On the other hand, Vonwiller obtained 4.5 for the ratio by using copper poles and currents of the same order as in this work, a result in good agreement with the value obtained here with silver poles.

Measurements were made with two arc currents, namely, 2 amp. and 4 amp. Table II shows the results obtained for each value of the current. It will be seen that the differences are well within the limits of error and it may therefore be assumed that absorption has a negligible effect.

[2] S. Sambursky, Zeits. f. Physik **49**, 731 (1928).

TABLE II. *Principal series doublets, $2s-mp_{1\frac{1}{2}}$, $2s-mp_{\frac{1}{2}}$.*

m	Wavelength	Arc current = 2 amp. No. of obs.	Mean (I_1/I_2)	Mean $(\overline{a_1^2}/\overline{a_2^2})$	Avg. err.	Prob. err.	Arc current = 4 amp. No. of obs.	Mean (I_1/I_2)	Mean $(\overline{a_1^2}/\overline{a_2^2})$	Avg. err.	Prob. err.
4	6549–6713A	3	4.3	3.9	0.5	0.3	5	5.4	4.9	0.7	0.35
5	5528–5583A	8	7.0	6.7	1.0	0.35	11	6.9	6.6	1.0	0.25
6	5109–5136A	11	6.0	5.9	0.8	0.2	11	6.15	6.0	1.0	0.25
7	4891–4906A	10	5.2	5.2	1.0	0.3	11	5.3	5.3	0.8	0.2

The average errors are high, but are not entirely due to the inaccuracy of measurement. The range of variation in each series of results obtained for the four doublets was about 50 percent of the mean value. However, the sets of values (about six), obtained from each plate were usually consistent to within 25 percent, there being noticeable changes from plate to plate. A recalculation of the results obtained for one doublet ($m=6$), showed that the photometry was accurate to within less than 10 percent. Apart from errors which may be involved in exposure and development, the large variation in results is to be attributed to changing conditions in the arc over which there is no direct control.

Since the material was at hand a calculation was made of the relative intensities of the stronger components of the doublets, $(2s-mp_{1\frac{1}{2}})$, from the second to the sixth members. Table III shows the results, the ratios given in column 4 being those of lines in adjacent doublets. In the fifth column the

TABLE III. *Relative intensities of stronger components, $2s-mp_{1\frac{1}{2}}$.*

m	Line	No. of obs.	Mean $I/_mI_{m+1}$	Mean $\overline{a^2}_m/\overline{a^2}_{m+1}$	Average error	Probable error	Ratio $\overline{a^2}_m/\overline{a^2}_{m-8}$
4	6549A	9	5.25	10.3	2.8	0.8	850
5	5528A	13	3.4	4.65	1.0	0.25	82
6	5109A	17	4.65	5.5	1.4	0.35	17.5
7	4891A	7	2.85	3.2	0.5	0.15	3.2
8	4768A						1
Weaker components							
6	5136A	12	3.6	4.3	1.3	0.35	
7	4906A						

ratios are given in terms of the mean squared amplitudes of the virtual oscillators. The errors in columns 6 and 7 refer to the numbers in column 5. In the last column are given the ratios of the mean squared amplitudes for each line to that for λ4768A. The logarithms of these last values have been plotted against m and are shown in Fig. 1. As with the doublet ratios no appreciable variation was found with change of arc current.

The mean of twelve observations of the relative intensities of the weaker components ($2s-mp_{1\frac{1}{2}}$), for $m=6$ and 7 has been used with the data given in Table I to provide an extra result for $m=6$.

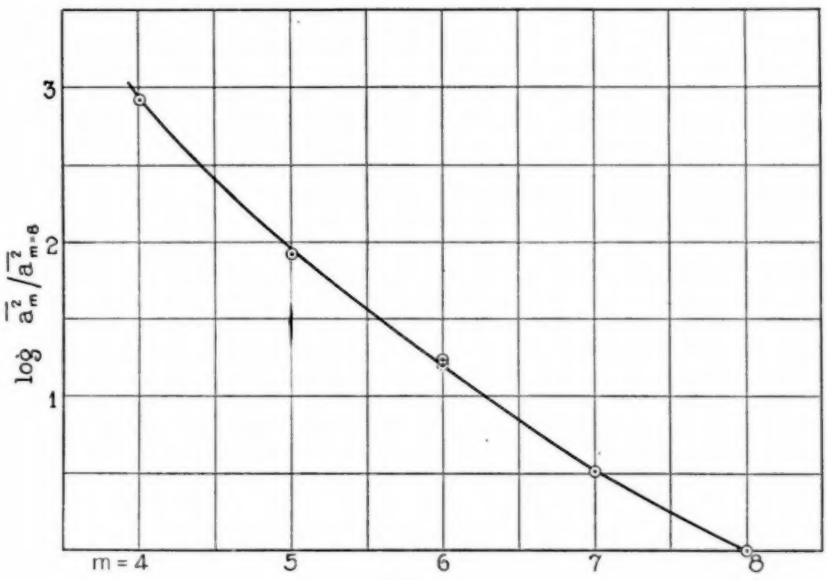

Fig. 1.

In conclusion we wish to express our thanks to the Cancer Research Department of the University of Sydney for the facilities granted in the use of the Moll microphotometer and especially to Professor O. U. Vonwiller for his help and advice in the carrying out of this work.

INTENSITIES IN SINGLET-TRIPLET BANDS OF DIATOMIC MOLECULES

By Robert Schlapp
University of Wisconsin
(Received January 13, 1932)

Abstract

Intensity formulae are found for the rotational structure of bands arising from transitions between a singlet and a triplet state of a diatomic molecule. These intercombinations occur because the wave functions which diagonalize the orbit-spin interaction contain both singlet and triplet terms. In the transition $^1\Sigma - {}^3\Sigma$ two cases arise, according as the two states have the same or opposite symmetry as regards reflection of the orbital motions in a plane containing the nuclei, a different set of branches appearing in either case. A comparison is made with measurements of intensities in the atmospheric absorption bands of oxygen; the agreement is satisfactory on the assumption that these bands are due to dipole transitions from the $^3\Sigma^-$ ground state to a $^1\Sigma^-$ state. Formulae are also found for the transitions $^1\Sigma - {}^3\Pi$, $^1\Sigma - {}^3\Delta$ when the triplet state comes under either of Hund's cases (a) or (b).

THEORETICAL investigations of intensities in electronic bands have hitherto dealt with transitions between states of the same multiplicity. Certain bands are however known from their structure to be due to "inter-system" combinations between terms of different multiplicities. In this paper only singlet-triplet combinations are considered, since all inter-system bands so far described are of this kind.

The proof of the selection rule for molecular spectra that only terms of like multiplicity combine depends on the possibility of separating the wave function of any state of the stationary molecule into the product of two factors, one depending on the orbital motions, and the other on the electron spins. This separation can be made only when the orbit-spin interaction is negligibly small; the effect of the interaction will be to modify the wave functions in such a way as to permit inter-system transitions of small intensity. In the analogous case of intercombinations between singlet and triplet terms in an atom with two electrons[1] it is necessary to solve this perturbation problem completely before the intensities can be calculated. The molecular problem is simpler in that for our purpose the perturbation problem need not be completely solved, nor indeed would this be possible without definite knowledge of the complete molecular wave functions. We are here concerned with the way in which the intensities depend on the rotation quantum number J for a given electronic transition, and not, as in the atomic case, with the intensities of different electronic transitions.

Stationary Molecule

Electronic orbital wave functions. The position of an electron with respect to the molecule with nuclei held fixed is specified by Cartesian coordinates

[1] W. V. Houston, Phys. Rev. **33**, 297 (1929).

($\xi\eta\zeta$) where ζ is along the axis of figure, or by cylindrical coordinates ($\rho\phi\zeta$), the azimuth ϕ about the ζ-axis being measured from the plane $\eta=0$. In analogy with the usual theory of the helium atom, the wave functions for a molecule with two electrons are, to a first approximation, of the form

$$p(1)e^{i\lambda_1\phi_1}q(2)e^{i\lambda_2\phi_2} \pm p(2)e^{i\lambda_1\phi_2}q(1)e^{i\lambda_2\phi_1}$$

where p, q, are real functions, supposed normalized, which do not involve ϕ_1 and ϕ_2, and λ_1, λ_2, are the components along the axis of figure of the orbital angular momenta l_1, l_2 of the individual electrons. The sum $\lambda_1+\lambda_2=\Lambda$ is equal to 1, 2, $\cdots$ for Π, Δ, $\cdots$ states, and the upper sign is appropriate for singlet states, the lower for triplets. If in virtue of the interaction between l_1 and l_2 the individual λ's are no longer good quantum numbers, the wave function is a linear combination of terms like the above all having the same value of $\lambda_1+\lambda_2=\Lambda$. In these wave functions, which are complex, there is a degeneracy associated with the two possible directions of orbital motion, corresponding to $\pm|\Lambda|$. If $\Lambda=0$ (Σ states), this degeneracy no longer exists. Since the coefficients of the wave equation are all real, the wave functions for Σ states are essentially real, and of the form $F\cos\lambda(\phi_1-\phi_2)$ or $G\sin\lambda(\phi_1-\phi_2)$ where F, G, are real functions of the coordinates of the electrons other than ϕ_1, ϕ_2. These two wave functions are respectively even and odd with respect to reflection of the orbital motion in the plane $\eta=0$ (replacement of ϕ by $-\phi$), and represent Σ^+ and Σ^- states.

Spin functions. For a singlet the spin function is, in the usual notation, $(\Phi_{\alpha_1}\Phi_{\beta_2}-\Phi_{\beta_1}\Phi_{\alpha_2})/2^{1/2}$ and for a triplet, $\Phi_{\alpha_1}\Phi_{\alpha_2}$, $(\Phi_{\alpha_1}\Phi_{\beta_2}+\Phi_{\beta_1}\Phi_{\alpha_2})/2^{1/2}$ or $\Phi_{\beta_1}\Phi_{\beta_2}$ according as the projection Σ of the total spin S on the axis of figure is equal to 1, 0, or -1. The sum $\Lambda+\Sigma$ is denoted by Ω, and is attached as a suffix to the term symbol.

Orbit-spin interaction. The unperturbed system to which these wave functions refer is specified by quantum numbers Λ, Σ and S. The energy H_0, including the energy of the electrons in the field of the nuclei, their electrostatic interaction, the coupling of orbits and spins separately to the axis of the molecule, and the "exchange" coupling energy of the two spins, is a diagonal matrix. We then take as the small perturbation the orbit-spin interaction $H_1=a_1(\mathbf{l}_1\cdot\mathbf{s}_1)+a_2(\mathbf{l}_2\cdot\mathbf{s}_2)$, where a_1, a_2, are real constants, $\mathbf{l}_1$ the vector with components $(l_1)_\xi=(h/2\pi i)(\eta_1\partial\cdots/\partial\zeta_1-\zeta_1\partial\cdots/\partial\eta_1)$ etc. and similarly for $\mathbf{l}_2$, and $\mathbf{s}_1$, $\mathbf{s}_2$ are the Pauli spin operators defined as usual.[2] It is readily verified by the properties of the operators $\mathbf{l}$ and $\mathbf{s}$ that the matrix H_1 involves terms for which $\Delta\Lambda=0$, ±1, and is diagonal in the quantum number Ω. The diagonality in Ω is otherwise obvious since the component of the total angular momentum along the axis of figure is a constant of the perturbed as well as the unperturbed motion.

The perturbed wave functions are therefore linear combinations of the unperturbed wave functions, all the functions in any combination having the same value of Ω, and multiplicities 1 or 3. To begin with we shall consider

[2] See, for example, J. H. Van Vleck, Phys. Rev. **33**, 467 (1929).

the most interesting case $^1\Sigma - {}^3\Sigma$ of inter-system combinations; the same method applies to other cases as well. In terms of the old wave functions ψ we have the following new wave functions ψ' for the Σ states:

$$\begin{aligned}
\psi'(^1\Sigma_0) &= a\psi(^1\Sigma_0) + p\psi(^3\Pi_0') + q\psi(^3\Sigma_0) + r\psi(^3\Pi_0) \\
\psi'(^3\Sigma_{-1}) &= b\psi(^3\Sigma_{-1}) + s\psi(^1\Pi_{-1}) \\
\psi'(^3\Sigma_0) &= c\psi(^3\Sigma_0) + t\psi(^1\Sigma_0) \\
\psi'(^3\Sigma_1) &= d\psi(^3\Sigma_1) + u\psi(^1\Pi_1)
\end{aligned} \tag{1}$$

where a, b, c, d, are constants of order unity, and p, q, r, s, t, u are constants much less than unity if, as we shall suppose, the orbit-spin interaction is small. In the wave functions for the triplet states terms in $\psi(^3\Pi)$ have been omitted, as they cannot contribute to the inter-system intensities $^1\Sigma - {}^3\Sigma$. The states denoted $^1\Pi_{-1}$ and $^3\Pi_0'$ have $\Lambda = -1$.

Rotating Molecule

To obtain the complete wave functions of the rotating molecule, each of the original ψ's must be multiplied by a function giving the vibrational motion of the nuclei along the line joining them, and by the appropriate symmetrical top function involving the quantum numbers J, Ω, M, in the usual way. As we are concerned with a definite vibrational level of each of the two states in question, the vibrational part of the wave function merely introduces a factor independent of J into the intensities, and may therefore be omitted in what follows. The symmetrical top function will be denoted by $u_{J\Omega M}(\theta, \omega)$. The Eulerian angles θ, ω, specify the orientation of the axes $(\xi\eta\zeta)$ with respect to axes fixed in space, θ being the angle between the ζ-axis and a preferential direction in space, taken as the z-axis, and ω giving the azimuth of the ξ-axis about the z-axis, to which it is supposed to remain perpendicular. We do not require the explicit expression of this function; the following property may be verified from the definition given by Van Vleck[2]

$$u_{J\Omega M}(\pi - \theta, \omega + \pi) = (-1)^J u_{J-\Omega M}(\theta, \omega). \tag{2}$$

Electric moment. We must now form the matrix elements of the components of the electric moment of the molecule, referred to axes fixed in space, and shall work with the z-component, for which $\Delta M = 0$. Denoting the amplitude for a transition from a rotational level J of a state X to a level J' of state Y by $(X-Y)(JJ')$, we have

$$\begin{aligned}
(^1\Sigma_0 - {}^3\Sigma_{-1})(JJ') &= as(^1\Sigma_0 - {}^1\Pi_{-1})(JJ') + br(^3\Pi_0 - {}^3\Sigma_{-1})(JJ') \\
(^1\Sigma_0 - {}^3\Sigma_0)(JJ') &= at(^1\Sigma_0 - {}^1\Sigma_0)(JJ') + cq(^3\Sigma_0 - {}^3\Sigma_0)(JJ') \\
(^1\Sigma_0 - {}^3\Sigma_1)(JJ') &= au(^1\Sigma_0 - {}^1\Pi_1)(JJ') + dp(^3\Pi_0' - {}^3\Sigma_1)(JJ').
\end{aligned} \tag{3}$$

If we remember that $z = \eta \sin\theta + \zeta \cos\theta$, we may write the following explicit expressions for the first terms on the right of these equations

$$as \int \psi^*(^1\Sigma_0)\eta\psi(^1\Pi_{-1})d\tau \int u^*_{J0M}u_{J'-1M} \sin^2\theta d\theta d\omega$$

$$at \int \psi^*(^1\Sigma_0)\zeta\psi(^1\Sigma_0)d\tau \int u^*_{J0M}u_{J'0M} \sin\theta\cos\theta d\theta d\omega$$

$$au \int \psi^*(^1\Sigma_0)\eta\psi(^1\Pi_1)d\tau \int u^*_{J0M}u_{J'1M} \sin^2\theta d\theta d\omega$$

where the integration $d\tau$ is over the positional coordinates of the two electrons in the stationary molecule, and includes summation over the spin coordinates. The integral over θ and ω is in each case the well-known amplitude factor for the symmetrical top. We denote the quotient of each of the above expressions by the modulus of the corresponding amplitude factor by A, B, C, respectively, so that A, B, C, are constants whose values depend on the internal dynamics of the molecule, and do not concern us, but whose relative phases for a given value of ΔJ are of importance in what follows.

The phases. Consider first the relation between the coefficients s, t, u, defined in equations (1). Since the off-diagonal terms of the energy matrix are much smaller than the diagonal terms, the phases of the elements $a, b, \cdots t, u$, of the transformation matrix arising in diagonalising H_0+H_1 are the same as those of the corresponding elements of H_0+H_1. Thus a, b, c, d, are all real. Remembering that with our choice of wave functions $\psi(^1\Pi_1) = \psi^*(^1\Pi_{-1})$ and that $\psi(^3\Sigma_1)$ and $\psi(^3\Sigma_{-1})$ are real, we readily find that the matrix elements of H_1 between $(^3\Sigma_1, {}^1\Pi_1)$ and $(^3\Sigma_{-1}, {}^1\Pi_{-1})$ are complex conjugates, so that $s=u^*$; also that if the triplet state is $^3\Sigma^+$, s is real, while if it is $^3\Sigma^-$, s is imaginary; t is always imaginary, and vanishes if both states have the same symmetry as regards reflection of the orbits alone in a plane containing the nuclei, i.e., the orbit-spin interaction will combine $^3\Sigma_0^+$ with $^1\Sigma^-$ but not with $^1\Sigma^+$.

If we denote the three integrals over the internal coordinates τ by l, m, n, respectively, we have $l=n^*$, and l is real or imaginary according as the singlet state is $^1\Sigma^-$ or $^1\Sigma^+$; m is always real.

In virtue of the integration over the coordinates θ, ω, and the property (2) of the symmetrical top function, A and C will differ by a factor $(-1)^{J+J'}$; the sign of B remains undetermined. Summing up we now have

$$A:B:C = sl:\pm tm:(-)^{J+J'}un = sl:\pm tm:(-)^{\Delta J}s^*l^*.$$

We therefore distinguish two cases:

$$\begin{aligned} &\text{(i)} && ^1\Sigma^+ - {}^3\Sigma^- \text{ or } {}^1\Sigma^- - {}^3\Sigma^+ : A = (-)^{\Delta J}C,\ B \neq 0 \\ &\text{(ii)} && ^1\Sigma^+ - {}^3\Sigma^+ \text{ or } {}^1\Sigma^- - {}^3\Sigma^- : A = (-)^{\Delta J+1}C,\ B = 0 \end{aligned} \qquad (4)$$

where A, B, C, are all real. A similar argument applied to the second terms on the right of equations (3) leads to the same result. Since the two transitions in any line of (3) have the same values of $\Delta\Omega$, ΔJ, ΔM, they depend on J in the same way, so that the form of the result (4) still holds when both

transitions are taken into account. In this section on phases we have made use of a model of the molecule which is somewhat specialised in that it has only two valence electrons. It is however reasonable to suppose that the phase relations are much more general than the model which was used to determine them.

The amplitudes. We now have the following scheme for the amplitudes of the three transitions ${}^1\Sigma_0 - {}^3\Sigma_{-1}$, ${}^1\Sigma_0 - {}^3\Sigma_0$, ${}^1\Sigma_0 - {}^3\Sigma_1$ for $\Delta M = 0$. The factors depending on J and M are taken from a paper by Kronig,[3] and are written so that J refers to the ${}^3\Sigma$ state.

$\Delta\Omega =$	-1	0	1
$\Delta J = -1$	$A[JQ(J+1)]^{1/2}$	$B[(J+1)Q(J+1)]^{1/2}$	$C[JQ(J+1)]^{1/2}$
0	$AM/[J(J+1)]^{1/2}$	0	$CM/[J(J+1)]^{1/2}$
1	$A[(J+1)Q(J)]^{1/2}$	$B[JQ(J)]^{1/2}$	$C[(J+1)Q(J)]^{1/2}$

(5)

where $Q(J) = (J^2 - M^2)/J(2J-1)(2J+1)$. In this table, which really represents two distinct cases (i) and (ii), the constants A, B, C, satisfy the relations (4).

Rotational Uncoupling of the Spin

In the rotating molecule, the ${}^3\Sigma$ state comes under Hund's case (b), in which the coupling between the spin and the axis of figure is negligible compared with that between the spin and the rotation of the molecule. The amplitudes given in the preceding table are not the actual amplitudes, but amplitudes for transitions between the ${}^1\Sigma$ state and a hypothetical ${}^3\Sigma$ state belonging to case (a), in which the spin is imagined as being firmly coupled to the axis of figure, so that the suffixes -1, 0, 1, in the ${}^3\Sigma$ state have a meaning as quantum numbers. To pass from these amplitudes to the actual amplitudes in which the ${}^3\Sigma$ state comes under case (b) we must consider the influence of the rotation in uncoupling the spin from the axis of figure.

The method of doing this has been given in a convenient form by Van Vleck,[2] who showed that the effect depends on a Hamiltonian function H, where

$$H(\Sigma; \Sigma \pm 1) = 2\beta[J(J+1) - \Omega(\Omega \pm 1)]^{1/2} s_\eta(\Sigma; \Sigma \pm 1)$$
$$H(\Sigma; \Sigma) = f(\Sigma) + \beta[J(J+1) + S(S+1) - \Omega^2 - \Sigma^2].$$

In these expressions β is the usual constant $h^2/8\pi^2 I$, and s_η is the η component of the Pauli operator for the total electron spin. The term $f(\Sigma)$ is the coupling energy between the total spin S and the axis of figure of the molecule, and is ordinarily proportional to $\Lambda\Sigma$. Here however we are interested in the case $\Lambda = 0$, $S = 1$; for this case Kramers[4] has shown that the interaction of the spins of the two electrons is equivalent to a coupling energy proportional to $(3\cos^2\chi - 1)$ between the spin and the axis of figure, χ being the angle between them. The matrix elements of this coupling energy are thus of the

[3] R. de L. Kronig, Zeits. f. Physik **45**, 458 (1927).
[4] H. A. Kramers, Zeits. f. Physik **53**, 422 (1929).

form $\alpha(2s_\zeta^2 - s_\xi^2 - s_\eta^2)$ where α is a constant which may be either positive or negative.

We now set up the secular determinant, noting that with our choice of ψ's the elements of s_η are imaginary. Strictly speaking we should calculate the matrix elements with respect to the wave functions ψ' of the stationary molecule, which take into account the orbit-spin interaction; but since the latter is small, we may without great error use the unperturbed functions ψ. The secular determinant is

$$\begin{vmatrix} J(J+1)+\lambda-w & -i[2J(J+1)]^{1/2} & 0 \\ i[2J(J+1)]^{1/2} & J(J+1)+2-2\lambda-w & -i[2J(J+1)]^{1/2} \\ 0 & i[2J(J+1)]^{1/2} & J(J+1)+\lambda-w \end{vmatrix}$$

where $\lambda = \alpha/\beta$, and is therefore large or small according as the state is nearly case (a) or case (b); and $w = W/\beta$. The secular equation may be solved accurately, the roots being

$$w = J(J+1)+\lambda,\quad J(J+1)+1-\lambda/2 \pm [(2J+1)^2 + 9\lambda^2/4 - 3\lambda]^{1/2}. \quad (6)$$

If we neglect λ altogether, the roots are $J(J-1)$, $J(J+1)$, $(J+1)(J+2)$. These give the rotational levels of the triplet belonging to a given value of J in case (b). Since in case (b) the energy is given mainly by $w = K(K+1)$ where K is the total angular momentum of the molecule exclusive of spin, we see that the three levels are distinguished by having $K = J-1$, J, $J+1$, respectively (T_1, T_2, T_3 terms in Mulliken's notation). If λ is so small that its square is negligible, we obtain for the levels the formulae which were obtained by Kramers. His unperturbed system consisted of a free rotator and a free spin vector, with the coupling between them as the perturbation; only those elements of the coupling energy were taken into account which are diagonal in K. This is a good approximation so long as the splitting of the levels caused by this perturbation is small compared with the rotational intervals, which is not always the case in practice. The exact formula (6) is not subject to this restriction; the terms in λ^2, $\lambda^3 \cdots$ may be looked on as giving the effect of the off-diagonal terms of the coupling which were neglected by Kramers.

In the neighborhood of case (a) $\lambda \gg 1$, and the roots of the secular equation are approximately λ, λ, -2λ; the root -2λ refers to the state ${}^3\Sigma_0$. Since the roots of the secular equation do not cross when the parameter λ changes from large negative to large positive values, we see that the (a) state ${}^3\Sigma_0$ passes into the (b) state $K = J-1$ or $K = J+1$ according as the coupling constant α is positive or negative. The correlation of the states ${}^3\Sigma_1$, ${}^3\Sigma_{-1}$, which have identical energies, with the two remaining (b) states cannot be determined by this argument. But since case (a) states are purely hypothetical when $\Lambda = 0$, the final intensity formulae must be independent of the correlation adopted between them and the actual (b) states. It is found that in oxygen the constant α is positive; we shall adopt the correlation ${}^3\Sigma_{-1} \sim {}^3\Sigma_J$, ${}^3\Sigma_0 \sim {}^3\Sigma_{J-1}$, ${}^3\Sigma_1 \sim {}^3\Sigma_{J+1}$, where we use the notation ${}^3\Sigma_{J-1}$, ${}^3\Sigma_J$, ${}^3\Sigma_{J+1}$ for the (b) states of ${}^3\Sigma$ usually denoted T_1, T_2, T_3.

For complete uncoupling of the spin ($\lambda=0$) the transformation matrix arising from the secular problem is

$$S=\begin{pmatrix} 1/2^{1/2} & 0 & 1/2^{1/2} \\ -[(J+1)/2(2J+1)]^{1/2} & i[J/(2J+1)]^{1/2} & [(J+1)/2(2J+1)]^{1/2} \\ [J/2(2J+1)]^{1/2} & i[(J+1)/(2J+1)]^{1/2} & -[J/2(2J+1)]^{1/2} \end{pmatrix}.$$

The columns refer to the (a) states ${}^3\Sigma_{-1}$, ${}^3\Sigma_0$, ${}^3\Sigma_1$ respectively, and the rows to the three (b) states ${}^3\Sigma_J$, ${}^3\Sigma_{J-1}$, ${}^3\Sigma_{J+1}$, in that order, with which we have correlated them. Each row may be multiplied by an arbitrary complex constant, which however does not affect the intensities. Here J refers to the ${}^3\Sigma$ state.

To pass from the amplitudes in the hypothetical transitions ${}^1\Sigma(a)-{}^3\Sigma(a)$ to the actual amplitudes ${}^1\Sigma(a)-{}^3\Sigma(b)$ it is necessary, as shown by Hill and Van Vleck,[5] to post-multiply the (a) amplitudes of (5) by S^*, so that for example the z-amplitude in the transition ${}^1\Sigma-{}^3\Sigma_J$ is given by the inner product of the appropriate row of the scheme (5) into the first row of S^*. This shows that the result is independent of the correlation; the quantum number of the hypothetical (a) state merely plays the part of an index of summation.

The following scheme gives the designations of the nine possible branches; the letters P, Q, R, are the usual symbols corresponding to $\Delta J=1,\ 0,-1$, and the upper left-hand affix gives the value of ΔK according to the same scheme, so that for example ${}^{RR}R$ means $\Delta J=-1$, $\Delta K=-2$.

$\Delta(K-J)$	${}^1\Sigma-{}^3\Sigma_{J-1}$ -1	${}^1\Sigma-{}^3\Sigma_J$ 0	${}^1\Sigma-{}^3\Sigma_{J+1}$ 1	
$\Delta J=-1$	${}^{RR}R$	${}^{R}R$	${}^{Q}R$	
0	${}^{R}Q$	${}^{Q}Q$	${}^{P}Q$	(7)
1	${}^{Q}P$	${}^{P}P$	${}^{PP}P$	

Instead of writing down the amplitudes, we shall content ourselves with giving the total intensities, which are obtained from the amplitudes for $\Delta M=0$ by taking three times the square of the modulus, and summing for all values of M from $-J$ to J. If we use the relations (4) between A, B, C, we find that in cases (i) and (ii) complementary sets of branches appear, whose intensities, arranged according to the preceding scheme, are as follows.

Case (i): Singlet and triplet states have opposite symmetry:

$$\begin{matrix} [2A^2+B^2]J(J+1)/(2J+1) & 0 & [2A^2J^2+B^2(J+1)^2]/(2J+1) \\ 0 & 2A^2(2J+1) & 0 \\ [2A^2(J+1)^2+B^2J^2]/(2J+1) & 0 & [2A^2+B^2]J(J+1)/(2J+1). \end{matrix}$$

Case (ii): Singlet and triplet states have the same symmetry:

$$\begin{matrix} 0 & 2A^2J & 0 \\ 2A^2(J+1) & 0 & 2A^2J \\ 0 & 2A^2(J+1) & 0. \end{matrix}$$

[5] E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928).

The appearance of complementary sets of branches in the two cases (i) and (ii) is in agreement with the selection rule that only states of opposite symmetry as regards reflection of nuclei and electrons in the origin can combine with each other. If as usual we call the two types of symmetry with respect to this reflection "positive" and "negative", the three component levels of a $^3\Sigma$ state belonging to a given value of K, and having $J=K+1$, K, $K-1$, all have the same symmetry, and are alternately positive and negative for successive values of K. Two possible cases arise, according as the states $^1\Sigma$, $^3\Sigma$ have (i) opposite, or (ii) the same symmetry, with regard to reflection in the origin, for a given value of K. These two cases are exactly equivalent to the two cases (i) and (ii) above, in which we considered symmetry as regards reflection of the orbits in a plane through the nuclei, since a Σ^+ state may alternatively be defined as one which is positive on reflection in the centre for even J, and a Σ^- state as one which is negative for even J. The nine possible branches fall into two sets, ${}^PP$, ${}^PQ$, ${}^RQ$, ${}^RR$, having ΔK odd, and ${}^{PP}P$, ${}^QP$, ${}^QQ$, ${}^QR$, ${}^{RR}R$, having ΔK even, and it is readily seen that the rule excluding transitions between states of like symmetry will exclude the first set or the second set in cases (i) and (ii) respectively.

Comparison with Experiment

There are no experimental data for the case in which the singlet and triplet states have opposite symmetry. According to one interpretation,[6] the atmospheric absorption bands of oxygen arise in transitions between a $^1\Sigma^-$ state and the $^3\Sigma^-$ ground state of the molecule; four branches are observed, which are classed as ${}^PP$, ${}^PQ$, ${}^RQ$, ${}^RR$. Reliable measurements of intensities are exceedingly difficult to make, but recently Childs and Mecke[7] have made a determination of intensities in the A bands of the absorption spectrum of atmospheric oxygen at room temperatures. The following table gives a comparison between the experimental results and those calculated above. The notation used by Childs and Mecke for the branches is different from that which has been adopted here; in the table both notations are given. We may observe in passing that there is no theoretical justification for the correlation of the triplet states which we have called $^3\Sigma_{J-1}$, $^3\Sigma_J$, $^3\Sigma_{J+1}$ with $^3\Sigma_{-1}$, $^3\Sigma_0$, $^3\Sigma_1$ respectively, which is the correlation adopted by Childs and Mecke. We have adhered to a more rational correlation, but the matter is not of importance, as we have shown above that the final result does not depend on the correlation. In the formulae of Childs and Mecke J refers to the singlet state; for the sake of comparison the calculated inten-

[6] R. S. Mulliken, Phys. Rev. **32**, 880 (1928). Mulliken's interpretation that the bands are $^1\Sigma^-_u - {}^3\Sigma^-_g$ is the usually accepted one. There are difficulties in accounting for the existence of the $^1\Sigma^-_u$ term in the oxygen molecule, and an alternative suggestion, also due to Mulliken, (Reviews of Modern Physics, Jan. 1931, on p. 96) is that the bands are quadrupole transitions $^1\Sigma^+_g - {}^3\Sigma^-_g$. Inter-system quadrupole intensities would of course be very weak indeed; the fact that we obtain good agreement between experiment and theory if we adopt Mulliken's first interpretation is evidence in its favour. See also, Rev. Mod. Phys. **4**, 1 (1932).

[7] W. H. J. Childs and R. Mecke, Zeits. f. Physik **68**, 344 (1931).

sities have been written in terms of this J instead of in terms of the J of the triplet state, as was done above.

Branch		Int. obs.	Int. calc.
${}^{P}P$	P_2	$(J+2)/2$	$(J+2)/2$
${}^{P}Q$	P_3	$(J+\frac{1}{2})/2$	$J/2$
${}^{R}Q$	R_1	$(J+\frac{1}{2})/2$	$(J+1)/2$
${}^{R}R$	R_2	$(J-1)/2$	$(J-1)/2$

The fact that in each branch only alternate lines are present is of course accounted for by the identity of the two nuclei and the absence of nuclear spin.

The agreement for the branches ${}^{P}P$ and ${}^{R}R$ is perfect; for ${}^{P}Q$ and ${}^{R}Q$ there is a discrepancy. Although the experiments just quoted are the most reliable that have so far been made, the actually observed intensities from which Childs and Mecke deduce the law of variation with J as given in the third column of the table show such considerable fluctuations that it is difficult to be certain about their interpretation.

In either of cases (i) and (ii) it is easily shown that the sum of the intensities of all lines having a given level J of the ${}^1\Sigma$ state in common is proportional to $2J+1$; also the sum of the intensities of all the lines having a given value of J in the ${}^3\Sigma$ states in common is proportional to $2J+1$; this value of J will in general occur in all three ${}^3\Sigma$ states, and the rule just given holds for the sum of the intensities from all levels of the triplet having the same J.

Intensities for ${}^1\Sigma-{}^3\Pi$, ${}^1\Sigma-{}^3\Delta$

When the triplet state is a Π or a Δ state, it may come under case (a) or case (b), or it may be intermediate between (a) and (b). We consider only the extreme cases. Consider first the three transitions ${}^1\Sigma-{}^3\Pi_0$, ${}^1\Sigma-{}^3\Pi_1$, ${}^1\Sigma-{}^3\Pi_2$, where the triplet state is case (a). The amplitude of the first transition is a linear combination of the amplitudes ${}^1\Sigma-{}^1\Sigma$ and ${}^3\Pi_0-{}^3\Pi_0$, the amplitude of the second is a linear combination of the amplitudes ${}^1\Sigma-{}^1\Pi_1$ and ${}^3\Sigma_0-{}^3\Pi_1$, while the amplitude of the third transition vanishes. It may easily be shown, by consideration of the wave functions, that the amplitudes ${}^1\Sigma-{}^3\Pi_0$ and ${}^1\Sigma-{}^3\Pi_1$ differ in phase by a factor i. The total intensities are given by the following table. D and E denote constants.

Branch	P	Q	R
${}^1\Sigma-{}^3\Pi_0$	$2D^2J$	0	$2D^2(J+1)$
${}^1\Sigma-{}^3\Pi_1$	$E^2(J+1)$	$E^2(2J+1)$	E^2J

To pass to the intensities when the ${}^3\Pi$ state comes under case (b) it is necessary to calculate the uncoupling matrix corresponding to the matrix S used above, and apply it to the amplitudes from which the intensities just written down were obtained. As before, nine branches are obtained, whose designations are given by the scheme (7), and whose intensities, arranged according to that scheme, are

$$\begin{array}{ccc} [D-E]^2(J+1)(J-1)/(2J+1) & [D(J+1)-E]^2/(J+1) & [D(J+1)+EJ]^2(J+2)/(2J+1)(J+1) \\ E^2(J+1)(J-1)/J & E^2(2J+1)/J(J+1) & E^2J(J+2)/(J+1) \\ [DJ-E(J+1)]^2(J-1)/J(2J+1) & [DJ-E]^2/J & [D+E]^2J(J+2)/(2J+1). \end{array}$$

If the triplet state is $^3\Delta$, case (a), the only component that can combine with $^1\Sigma$ is $^3\Delta_1$. The amplitude is then a linear combination of the amplitudes $^1\Sigma - {}^1\Pi_1$ and $^3\Pi_0 - {}^3\Delta_1$, and the total intensity is, apart from a constant factor.

Branch	P	Q	R
$^1\Sigma - {}^3\Delta_1$	$J+1$	$2J+1$	J

The intensities of the nine branches arising when the state is case (b) are

$$\begin{array}{ccc} (J+2)(J+3)/(2J+1) & (J-2)(J+3)/(J+1) & J(J-1)(J-2)/(J+1)(2J+1) \\ (J+2)(J+3)/J & (J-2)(J+3)(2J+1)/J(J+1) & (J-1)(J-2)/(J+1) \\ (J+1)(J+2)(J+3)/J(2J+1) & (J-2)(J+3)/J & (J-1)(J-2)/(2J+1). \end{array}$$

In all the formulae of this section J refers to the triplet state. To obtain the formulae in terms of J' referring to the singlet state, it is necessary to replace J by $J'+1$, J', $J'-1$, in expressions relating to P, Q, and R branches respectively. In every case it is readily shown that for a given J or J' the sum of all the intensities is proportional to $2J+1$ or $2J'+1$.

It is a pleasure to acknowledge the continued helpful interest of Professor J. H. Van Vleck in this work, and to thank Professor Mulliken for the opportunity of discussion.

THE EFFECT OF PRESSURE UPON THE e.m.f. OF THE WESTON STANDARD CELL

By Thos. C. Poulter and Carter Ritchey
Physics Laboratory, Iowa Wesleyan College

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Abstract

Several specially designed Weston Standard Cells have been constructed and subjected to large hydrostatic pressures. The cell cases were made of glass, beeswax, or rubber and the e.m.f. measured at pressures from 1 to 12,000 atmospheres. Such pressures have the effect of increasing the e.m.f. only by a small percent.

Introduction

THE effect of pressure upon the e.m.f. of a large number of electric cells has been studied by Ernst Cohen and his co-workers. Most of this work is done at pressures below 1,500 atmospheres. In 1909 E. Cohen and L. R. Sinnige[1] published some articles in which they calculated the change in solubility of cadmium sulphate from the change in the e.m.f. of the Weston Standard Cell as the pressure was varied from 1 to 1000 atmospheres. It is the purpose of this investigation to measure the effect of much higher pressures upon the e.m.f. of this cell.

Apparatus and Procedure

For this purpose two different types of pressure equipment were used. One is a vertical type cylinder with an electrode insulated through the bottom of the cylinder and the other has a horizontal chamber at the end of the pressure cylinder through the end of which an electrode is insulated. These cylinders are shown in Figs. 1 and 2.

The vertical cylinder has an inside diameter of 16 mm and is drawn to scale. The pressures are developed by forcing the piston in with a hydraulic press. Leakage around the piston B was prevented by means of the close fitting rubber stopper E placed just ahead of it. The applied pressure causes it to be forced tightly against the cylinder walls. The pressure in the high pressure cylinder was determined by multiplying the pressure in the press cylinder by the ratio of the diameter of the two pistons. This pressure is then corrected for the friction[2] of the two pistons. The electrode F is insulated from

[1] Ernst Cohen and L. R. Sinnige, Trans. Faraday Soc. **5**, 269 (1909); Zeits. f. physik. Chemie **67**, 536 (1909).

[2] The packing used in the hydraulic press cylinder is a self-acting leather packing which offers a friction of less than 0.5 percent of the total force. Houghton Research Staff, Hydraulic Engineering p. 48–49 (1926). The friction of the small piston was determined by means of a cylinder having a piston in each end. The friction is then determined by measuring the force necessary to move the cylinder on the pistons while under pressure. The corrected values checked closely with those obtained by the manganin wire resistance method.

the walls of the cylinder by the fiber shell *I* and from the bottom of the cylinder by the mica disc *J*. For use in this type of pressure apparatus the Weston Standard Cell was constructed in the form of a cylinder 12 mm in diameter and 40 mm long. One terminal is connected to the electrode *F* which is insulated through the bottom of the apparatus. The other is grounded to the piston and thereby to the entire assembly. The cell case *P* was made of

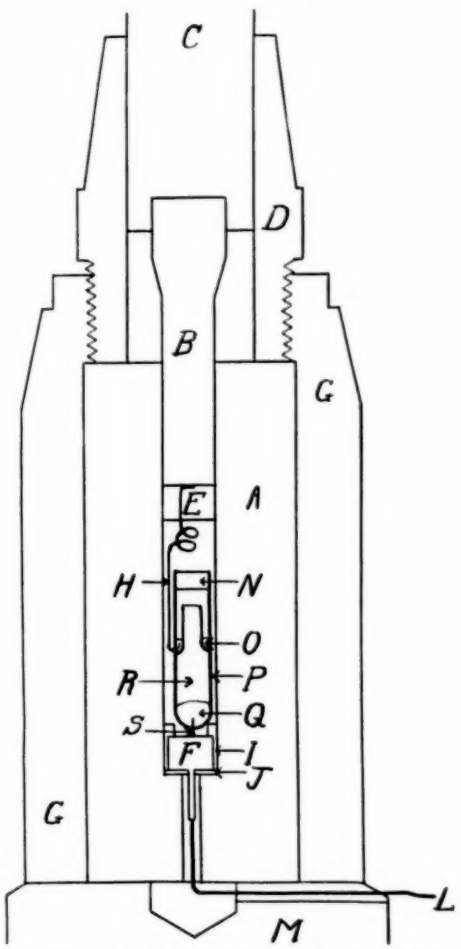

Fig. 1. Pressure cylinder with Weston Standard Cell in place.

glass or beeswax. The cadmium amalgam *Q* is connected to the electrode *F* by means of the platinum wire *S*. The platinum electrode *H* connects the mercury *O* to the piston. The cadmium sulphate solution *R* completely fills the cell case which is closed by means of a rubber stopper *N*. The surrounding space in the cylinder is filled with a light paraffin oil. Cells of this type made of glass served very well for pressures up to 5000 or 6000 atmospheres. At higher pressures glass cells would usually be broken. A number of successful measurements were made with cells constructed of beeswax at pressures of as high as 8000 atmospheres.

At this point in the investigation the other type pressure cylinder Fig. 2 was used which necessitated the use of a horizontal instead of a vertical cell. To meet these requirements a cell case was constructed from 6 mm inside diameter rubber tubing *P*. The two ends of the tube are closed with rubber stoppers *O* each carrying a platinum electrode. The space *N* contains the cadmium amalgam and *L* contains the mercury. The mercury and amalgam are kept separated by means of the two porous porcelain plugs *J*. The space *K* and the pores of the porcelain are filled with the cadmium sulphate solution. One terminal of this cell was connected to the electrode *F* insulated through the end of the cylinder and the other grounded to the cylinder. Readings were made by means of a potentiometer with the cylinder at 20°C and 30°C. This cylinder is not equipped with a water jacket for temperature con-

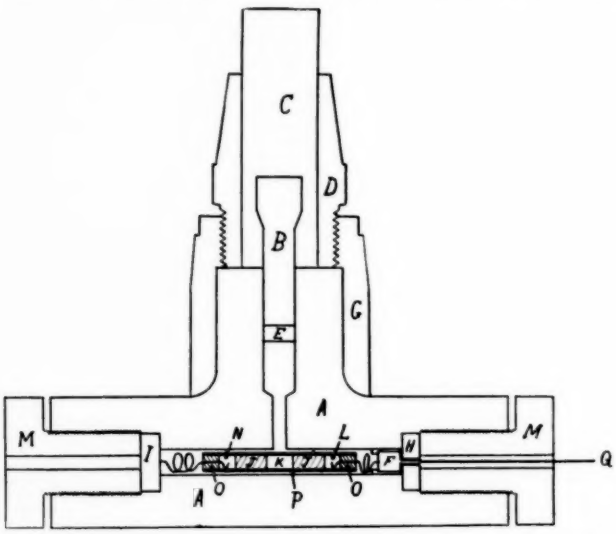

Fig. 2. Pressure cylinder with Weston Standard Cell in place.

trol as was the case in later work so that the temperature may have varied slightly from these values. In most cases readings were taken as the pressure was being increased and again as it was being decreased. The difference between the two sets of data thus obtained was usually not more than 0.001 volt. Five minutes was allowed following a pressure change for the cell to come to equilibrium. Typical sets of data are shown in Fig. 3 for 20°C and 30°C. The values obtained for this cell by Cohen and Sinnige up to 1000 atmospheres are represented by crosses in the figure.

Discussion of Results

It will be noticed from Fig. 3 that an increase in pressure of 12,000 atmospheres produces an increase of only 0.05 volts which is only about five percent of the original value.

The chemical reaction in the Weston Standard Cell can be represented by the following equation.

$$\underset{\text{Solid}}{Cd} + \underset{}{Hg_2SO_4} + (8/3)H_2O \rightarrow \underset{\text{Solid}}{CdSO_4 \cdot (8/3)H_2O} + 2Hg.$$

For this reaction to be affected directly by pressure there must be a change of volume due to the chemical changes or a difference in compressibility of the materials on the two sides of the equation.

Calculating the change in volume for the passage of one faraday of electricity at atmospheric pressure we find that the volume of the materials on the left-hand side is 111.78 cm³ (12.99, Cd+50.75, Hg_2SO_4+48.03, (8/3) H_2O=111.78), whereas the volume on the right-hand side is 112.71 cm³ (83.09, $CdSO_4$ (8/3)H_2O+29.62, 2Hg=112.71). This makes a change in

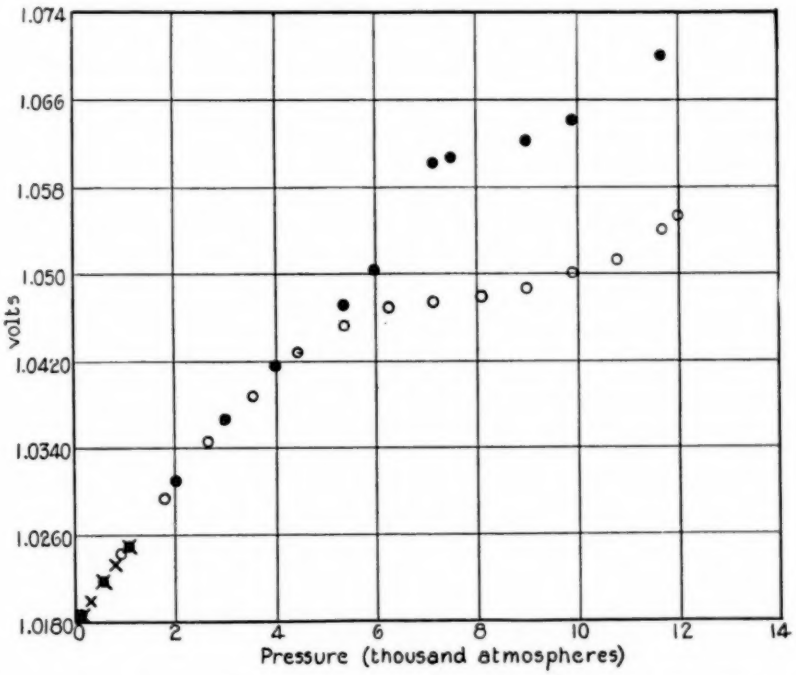

Fig. 3. Effect of pressure upon the e.m.f. of the Weston Standard Cell at 20°C and 30°C. Circles values at 20°C. Black dots, values at 30°C. Crosses, values obtained by Cohen and Sinnige.

volume of only 0.93 cm³ due to the chemical reaction. Since this is an increase in volume, its effect when pressure is applied should be to decrease the potential.

If the compressibility of the materials on one side of the chemical equation is greater than it is for the materials on the other side, an increase in pressure will tend to shift the reaction in the direction of the greater compressibility. The compressibility is known for cadmium, mercury and water but not for the other constituents so that predictions as to the magnitude or direction of this effect is impossible until more data are available.

The concentration of the saturated cadmium sulphate solution may be

effected in two ways by pressure. First, the increase in solubility with pressure because the volume of the solution is less than the combined volumes of the solute and the solvent, and second, the increase in hydration with pressure which in turn increases the solubility. The following hydrates of cadmium sulphates are known: $CdSO_4(1/2)H_2O$, $CdSO_4 1\ H_2O$, $CdSO_4(3/2)\ H_2O$, $CdSO_4(8/3)\ H_2O$, $CdSO_4(5/2)\ H_2O$, $CdSO_4\ 4H_2O$, $CdSO_4\ 7H_2O$, and $CdSO_4\ 9H_2O$. The solubility of the higher hydrates is more than double that of the lower hydrates. The effect of pressure upon the concentration of the cadmium sulphate is, therefore, probably rather large.

Another important factor is the polymorphic modifications of the various constituents as produced by high pressure. Cadmium exists in three solid and one liquid modification, mercury in one solid and one liquid and water in five solid and one liquid. Not all of these exist at conditions employed in this investigation, however, three for Cd, two for Hg, and two for H_2O are probably influential in changing the potential. The difference in the values for the two temperatures as shown in Fig. 3 is about what would be expected if they were produced by the formation of a polymorphic modification of some of the constituents. For instance, in the case of water or mercury an increase of ten degrees in temperature makes it necessary to apply an additional pressure of 2000 atmospheres to form the solid modification.

Summary

There is, therefore, likely the following factors affecting the potentials of this cell.

1. Increase in volume due to chemical reaction.
2. Increase solubility with pressure
   (*a*) due to decrease in volume on dissolving.
   (*b*) due to increase hydration with pressure.
3. Difference in compressibility on opposite sides of the chemical equation.
4. Change in physical states due to pressure.
   (*a*)Cd 3 modifications
   (*b*)Hg 2 modifications
   (*c*)H_2O 2 modifications

Since few or no data are available for some of these factors at such high pressures no attempt is made to predict the effect.

KINETIC INTERPRETATION OF THE KELVIN RELATIONS

By E. A. Uehling
Department of Physics, University of Michigan

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Abstract

The derivation of the Kelvin relations for the reversible heat development and the thermo-electric force in crystals is shown to depend only on the assumption of the principle of detailed balancing. Previous treatments of this subject have been less general. The work of Nordheim is valid only for isotropic materials, and that of Ehrenfest and Rutgers, though applicable to crystals, depends on the assumption of elastic collisions between the electrons and the atoms of the metal. In both treatments the electrons are assumed to be completely free and to be described by an energy function which is spherically symmetrical. All of these restricting assumptions are removed. The solution of the integral equation describing the distribution function of the electrons is obtained by a general method which depends only on the assumption of detailed balancing. This principle gives the integral equation an essentially symmetrical kernel, as a consequence of which a formal solution may be obtained. One may use this solution to derive the electric and heat current equations and to prove certain reciprocal relations from which the Kelvin equations follow. The proof of the existence of these relations, involving as it does only the assumption of detailed balancing, may be considered as a substantiation for the case of conduction in metals of certain very general considerations of Onsager.

§1. Introduction

A KINETIC derivation of the Kelvin relations for the reversible heat development and the thermo electric-force in metals has been given by Nordheim[1] for isotropic materials and by Ehrenfest and Rutgers[2] for crystals. In addition to the principle of detailed balancing which plays an essential role in all kinetic interpretations the following assumptions have been used: (a) Both treatments make use of an energy function which in terms of wave numbers or of the electron velocities is spherically symmetrical. This is equivalent to the assumption that the electrons are completely free. (b) Nordheim makes assumptions that restrict the application of his conclusions to isotropic materials. (c) Ehrenfest and Rutgers consider crystals as well as isotropic materials, but they introduce the restricting assumption of elastic collisions between the electrons and the ions of the crystal lattice. Both treatments are entirely general with respect to statistics.[3]

[1] L. Nordheim, Ann. d. Physik, [5], **9**, 607 (1931). Zur Elektronentheorie der Metalle. I, II.

[2] P. Ehrenfest und A. J. Rutgers, Proc. Kon. Acad. Amst. **32**, 698, 883 (1929). Zur Thermodynamik und Kinetik der thermoelektrischen Erscheinungen in Krystallen, insbesondere des Bridgman-Effektes. II. A. J. Rutgers, Dissertation Leiden, 1930.

[3] Independence of statistics is obtained by using the function:

$$f_0 = g(Ae^{-\epsilon/KT}) \tag{1}$$

to describe the equilibrium distribution of the electron energies. In this equation ϵ is the total energy of an electron in a certain cell in momentum space, f_0 represents the number of electrons

The author proposes to show that the restricting assumptions *a*, *b*, and *c* are unnecessary, and that *a derivation of the current equations and the Kelvin relations can be given when one retains only the principle of detailed balancing.*

§2. The Electric and Heat Current Equations

Using the special assumptions described, Nordheim obtains the following equations for the electric and heat currents in an isotropic material:

$$i_x = eK_1\left(eF_x - \frac{KT}{A}\frac{\partial A}{\partial x}\right) - \frac{eK_2}{T}\frac{\partial T}{\partial x} \tag{2}$$

$$w_x = K_3\left(eF_x - \frac{KT}{A}\frac{\partial A}{\partial x}\right) - \frac{K_4}{T}\frac{\partial T}{\partial x} \tag{3}$$

where F_x is the electric field, $\partial T/\partial x$ is the temperature gradient, K is the Boltzmann constant, and A is the coefficient in the distribution function (1). The four coefficients, K_1, K_2, K_3 and K_4 are functions of the temperature and the coordinates, and they depend, furthermore, upon a function which describes the behavior of the electrons in collisions, and upon the choice of statistics. Among these coefficients Nordheim finds the important *reciprocal relation*

$$K_2 = K_3. \tag{4}$$

The validity of the Kelvin relations is shown to depend upon the existence of this condition.

Ehrenfest and Rutgers, using the special assumptions described, obtain the following equations for the electric and heat conduction currents in anisotropic crystals:

$$i_s(x_1x_2x_3) = eK_{rs}^{(1)}\left[eF_r - \frac{KT}{A}\frac{\partial A}{\partial x_r}\right] - \frac{eK_{rs}^{(2)}}{T}\frac{\partial T}{\partial x_r} \tag{5}$$

$$w_q(x_1x_2x_3) = eK_{rq}^{(2)}\left[eF_r - \frac{KT}{A}\frac{\partial A}{\partial x_r}\right] - \frac{K_{rq}^{(3)}}{T}\frac{\partial T}{\partial x_r} \tag{6}$$

where the appearance of a letter twice as an index in a single term indicates a summation for that letter over the numbers 1, 2, and 3. The three coefficients are symmetrical tensors which are functions of position and temperature, and which depend, furthermore, upon the nature of the function which describes electron transitions in collision, and upon the choice of statistics. The *reciprocal relation* existing between the two current equations is in this case the appearance of the same coefficient $K_{rp}^{(2)}$ in both equations. Since it is symmetrical

$$K_{rp}^{(2)} = K_{pr}^{(2)}. \tag{7}$$

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in such a cell, T is the absolute temperature, K is the Boltzmann constant, and A is a coefficient depending on temperature and position, which is determined by setting the sum of f_0 over all cells of momentum space equal to the total number of electrons. The form of the function g depends on the choice of statistics.

This condition is essential in the derivation of the Kelvin relations from the current equations.

Assuming only the principle of detailed balancing one obtains the following equations for the electric and heat currents in crystals:

$$i_s(x_1x_2x_3) = eK_{rs}^{(1)}\left[eF_r - \frac{KT}{A}\frac{\partial A}{\partial x_r}\right] - \frac{eK_{rs}^{(2)}}{T}\frac{\partial T}{\partial x_r} \tag{8}$$

$$w_q(x_1x_2x_3) = K_{rq}^{(3)}\left[eF_r - \frac{KT}{A}\frac{\partial A}{\partial x_r}\right] - \frac{K_{rq}^{(4)}}{T}\frac{\partial T}{\partial x_r}. \tag{9}$$

These equations differ from those of Ehrenfest and Rutgers in the meaning of the tensor coefficients and in the existence of four such functions instead of three. Unlike the tensors $K_{rp}^{(2)}$ of Ehrenfest and Rutgers, *the coefficients* $K_{rs}^{(2)}$ *and* $K_{rq}^{(3)}$ *are not, in general, symmetrical in their indices.*[4] Nevertheless, one may show that under all conditions the reciprocal relation:

$$K_{rq}^{(2)} = K_{qr}^{(3)} \tag{10}$$

exists between these equations. The other two coefficients $K_{rs}^{(1)}$ and $K_{rq}^{(4)}$ are always symmetrical in their indices. These conditions are just sufficient for the derivation of the Kelvin relations.[5]

Conditions (4), (7) and (10), which have been found to exist in the three different treatments of this subject, are special cases of a general class of such relations. Onsager,[6] who has considered irreversible phenomena in general, finds that one may demonstrate the existence of reciprocal relations of this kind between any two processes which are not independent if the principle of detailed balancing is assumed. The conclusions described above may be taken as a substantiation for the case of conduction in metals of these more general and rather abstract considerations.

§3. General Method

The foundation of these derivations is the well-known Boltzmann equation for the distribution function f of the electrons. This equation may be written in the form:

[4] The explicit form of these tensors which is to be given later shows that they are symmetrical in their indices only when the function representing the total energy of the electron is separable in three terms, each of which depends on a single quantum number and is the same function of its argument as each of the other two; i.e., the energy must be of the form:

$$\epsilon = f(k_1) + f(k_2) + f(k_3).$$

Since it may rarely, if ever, be possible to express the energy for any actual metal in this form, the coefficients $K_{rs}^{(2)}$ and $K_{rq}^{(3)}$ of the current equations are not, in general, symmetrical.

[5] Since the current equations have been derived under the single assumption of detailed balancing with all restricting assumptions removed, these relations may be considered as the necessary and sufficient conditions upon which the validity of the Kelvin relations is based. As is to be expected, these conditions are in general weaker than those found by Ehrenfest and Rutgers and by Nordheim.

[6] Lars Onsager, Phys. Rev. **37**, 405–426 (1931). Reciprocal Relations in Irreversible Processes. I.

$$X_r \frac{\partial f}{\partial \xi_r} + \xi_r \frac{\partial f}{\partial x_r} = \iiint w(P'P) f(P') [1 + \theta f(P)] dk_1' dk_2' dk_3' - \iiint w(PP') f(P) [1 + \theta f(P')] dk_1' dk_2' dk_3' \tag{11}$$

where X_r is the rth component of the acceleration of an electron, ξ_r is the rth component of the mean velocity of drift, $w(PP')$ is a function describing the transition probability of an electron in a cell P of momentum space to a cell P', k_r is the quantum wave number in the rth direction of space, and θ has the value 1, 0, or -1 depending on whether the choice of statistics is Einstein-Bose, Maxwell-Boltzmann, or Fermi-Dirac. Introducing the principle of detailed balancing:

$$f_0(P) [1 + \theta f_0(P')] w(PP') = f_0(P') [1 + \theta f_0(P)] w(P'P) \tag{12}$$

one obtains a relation between the probabilities of the direct process ($P \rightarrow P'$) and the restituting process ($P' \rightarrow P$) which for all statistics is given by the equation:

$$w(PP') e^{\epsilon'/KT} = w(P'P) e^{\epsilon/KT} = W(PP') = W(P'P). \tag{13}$$

The new function $W(PP')$ defined by this equation is obviously symmetrical in all of the primed and unprimed variables on which it depends. Since no further assumptions have been made, it must be considered as a function of all the variables by which a cell in momentum space is specified and, in general, of the coordinates as well. Then it may be written as $W(x_1 x_2 x_3 k k' a_1 a_2 a_3 a_1' a_2' a_3')$ where $x_1 x_2 x_3$ are the coordinates, k the absolute magnitude of the wave number, and $a_1 a_2 a_3$ the direction cosines of the electron velocity.[7] The introduction of this function into the Boltzmann equation eliminates the unsymmetrical probability function from the equation and gives the foundation for the further treatment which is to follow.

One attempts to solve this equation by writing:

$$f = f_0 + f_1 \tag{14}$$

where f_1 is a small perturbation term. Introducing Eqs. (13) and (14) into Eq. (11), neglecting second order terms, and writing x for $x_1 x_2 x_3$ and a for $a_1 a_2 a_3$ one obtains:

$$X_r \frac{\partial f_0}{\partial \xi_r} + \xi_r \frac{\partial f_0}{\partial x_r} = \int d\phi' W(x k k' a a') \left[\frac{f_0 f_1'}{f_0'} e^{-\epsilon'/KT} - \frac{f_0' f_1}{f_0} e^{-\epsilon/KT} \right] \tag{15}$$

where $d\phi' = dk_1' dk_2' dk_3'$. This equation is to be solved for the unknown perturbation function f_1. Various methods of accomplishing this result, which are possible when certain restricting assumptions are made, have been used

[7] An essential difference in the three treatments exists at this point. Nordheim, considering isotropic materials, writes the probability function as $w(x_1 x_2 x_3 k k' \theta)$ where θ is the angle between the vectors representing k and k'. Ehrenfest and Rutgers, considering crystals but assuming that all electron collisions are elastic, write w as $w(x_1 x_2 x_3 v; a_1 a_2 a_3 a_1' a_2' a_3')$.

in the previous theoretical treatments of conduction in metals.[8] When no such assumptions are made, a very general method of solution, according to which the unknown function is formally expressed in terms of a symmetrical solving function $S(xkk'aa')$ must be used. This method, like all others, depends essentially on the principle of detailed balancing, but, unlike these other methods, it requires no restricting assumptions of any kind.

§4. Formal Solution of the Integral Equation; Determination of the Electric and Heat Current Equations

The left member of the integral equation must be written in terms of wave numbers before a solution can be obtained. The foundation of this transformation is the Peierls theorem[9] which relates the mean velocity of drift of an electron through a crystal lattice to the differential quotient of its total energy with respect to the wave number:

$$\xi_r = \frac{L}{h}\frac{\partial \epsilon}{\partial k_r} \tag{16}$$

where L is the length of the crystal, and h is Planck's constant. Using this theorem one obtains for electrons of any degree of binding subjected to an external electric field of components F_r, ($r = 1$, 2, and 3).

$$X_r = eF_r \frac{L}{h}\frac{\partial \xi_r}{\partial k_r} \tag{17}$$

$$\frac{\partial f_0}{\partial \xi_r} = \frac{h}{L}\xi_r \frac{\partial f_0}{\partial \epsilon} \Big/ \frac{\partial \xi_r}{\partial k_r} \tag{18}$$

[8] Nordheim, using a method of solution introduced by Lorentz, writes f_1 as the product of two functions:

$$f_1 = k \cos\theta \chi(k) = k_x \chi(k)$$

where k is the absolute magnitude of the wave number, and θ is the angle between the direction of the electron velocity and the direction of the potential and temperature gradients. The equation in f_1 is reduced in this manner to an equation in $\chi(k)$ which may be solved by general methods. The assumption that f_1 is a function of this form is easily justified when the fundamental equation is descriptive of processes in isotropic media, but not otherwise, for it is only in such materials that the heat and electric currents can be assumed to have the same direction as the temperature and potential gradients. Ehrenfest and Rutgers obtain a solution in the anisotropic case by writing the perturbation function as

$$f_1 = P_r(xv) \cdot G_r(xv; a_1 a_2 a_3)$$

where $P_r(xv)$ is the coefficient of a_r in the left member of the Boltzmann equation, and the functions $G_r(xv; a_1 a_2 a_3)$, where r has the values 1, 2, and 3, are the solutions of the three integral equations into which the original one is decomposed. This method of solution is possible only when the absolute magnitude of the electron velocity v, or its corresponding wave number k, is not one of the integration variables. It cannot be used, therefore, when the assumptions of Ehrenfest and Rutgers are not made.

[9] This theorem has been proved by R. Peierls (Zeits. f. Physik **53,** 255 (1929), Zur Theorie der galvanomagnetischen Effekte) for nearly free electrons. It is valid, however, for electrons of all degrees of binding. A general proof of the theorem has been received from J. R. Oppenheimer in a communication by letter to G. E. Uhlenbeck.

$$X_r \frac{\partial f_0}{\partial \xi_r} = eF_r \xi_r \frac{\partial f_0}{\partial \epsilon} \tag{19}$$

Also

$$\frac{\partial f_0}{\partial x_r} = -\frac{\partial f_0}{\partial \epsilon}\left[\frac{KT}{A}\frac{\partial A}{\partial x_r} + \frac{\epsilon}{T}\frac{\partial T}{\partial x_r}\right] \tag{20}$$

for all statistics. Then the left member of the integral equation becomes:

$$\xi_r \frac{\partial f_0}{\partial \epsilon}\left[eF_r - \frac{KT}{A}\frac{\partial A}{\partial x_r} - \frac{\epsilon}{T}\frac{\partial T}{\partial x_r}\right] \tag{21}$$

$$= u_r \frac{\partial f_0}{\partial \epsilon}[P_r(x_1x_2x_3) + \epsilon Q_r(x_1x_2x_3)] \tag{22}$$

where

$$P_r(x_1x_2x_3) = eF_r - \frac{KT}{A}\frac{\partial A}{\partial x_r} \tag{23}$$

$$Q_r(x_1x_2x_3) = -\frac{1}{T}\frac{\partial T}{\partial x_r} \tag{24}$$

and u_r is the mean velocity of drift considered as a completely arbitrary function of all the quantum numbers.

Now define a new function g_1 by means of the equation

$$f_1 = -\frac{\partial f_0}{\partial \epsilon} g_1 = \frac{f_0^2}{AKT} e^{\epsilon/KT} g_1. \tag{25}$$

Introducing this function into the integral Eq. (15), using expression (22) for the left member, and multiplying both members by k^2, one obtains

$$\begin{aligned} &f_0^2 e^{\epsilon/KT} k^2 u_r [P_r(x) + \epsilon Q_r(x)] \\ &= g_1 \int_{k'} k^2 k'^2 dk' \int_{w'} d\omega' W(xkk'aa') f_0 f_0 \\ &\quad - \int_{k'} k^2 k'^2 dk' \int_{w'} d\omega' W(xkk'aa') g_1' f_0 f_0'. \end{aligned} \tag{26}$$

The kernel of this integral equation is symmetrical in all primed and unprimed variables, since $W(xkk'aa')$ is symmetrical in these variables. Then a formal solution containing a symmetrical solving function may be obtained directly. This solution is:

$$\begin{aligned} g_1(xka) = &\frac{f_0^2 e^{\epsilon/KT} k^2 u_r P_r(x)}{H(ka)} + \frac{f_0^2 e^{\epsilon/KT} k^2 u_r \epsilon Q_r(x)}{H(ka)} \\ &+ \int dk' \int d\omega' \frac{f_0'^2 e^{\epsilon'/KT} k'^2 u_r' P_r(x)}{(H(k'a')H(ka))^{1/2}} S(xkk'aa') \end{aligned} \tag{27}$$

$$+ \int dk' \int d\omega' \frac{f_0'^2 e^{\epsilon'/KT} k'^2 u_r' \epsilon' Q_r(x)}{(H(k'a')H(ka))^{1/2}} S(xkk'aa')$$
$$= P_r(x)G_r(xka) + \epsilon Q_r(x)J_r(xka) \tag{28}$$

where

$$G_r(xka) = \frac{f_0^2 e^{\epsilon/KT} k^2 u_r}{H(ka)} + \int dk' \int dw' \frac{f_0'^2 e^{\epsilon'/KT} k'^2 u_r'}{(H(k'a')H(ka))^{1/2}} S(xkk'aa') \tag{29}$$

$$J_r(xka) = \frac{f_0^2 e^{\epsilon/KT} k^2 u_r}{H(ka)} + \int dk' \int dw' \frac{f_0'^2 e^{\epsilon'/KT} k'^2 u_r'}{(H(k'a')H(ka))^{1/2}} \frac{\epsilon'}{\epsilon} S(xkk'aa')$$

$$H(xka) = \int k^2 k'^2 dk' \int d\omega' W(xkk'aa') f_0 f_0' \tag{31}$$

and $S(xkk'aa')$ is the symmetrical solving function.

The first order perturbation term f_1 is obtained from this expression for g_1, and the electron and heat current equations are obtained by introducing this expression for f_1 into the equations:

$$i_s = \frac{Ge}{L^3} \int\int\int u_s f_1 dk_1 dk_2 dk_3 \tag{32}$$

$$w_q = \frac{G}{L^3} \int\int\int u_q \epsilon f_1 dk_1 dk_2 dk_3. \tag{33}$$

One obtains:

$$f_1 = -\frac{\partial f_0}{\partial \epsilon} \{P_r(x)G_r(xka) + \epsilon Q_r(x)J_r(xka)\} \tag{34}$$

$$i_s(x_1x_2x_3) = -\frac{Ge}{L^3} \int k^2 P_r(x)\Gamma_{rs}(xk)dk - \frac{Ge}{L^3} \int k^2 Q_r(x)\Lambda_{rs}(xk)dk \tag{35}$$

$$w_q(x_1x_2x_3) = -\frac{G}{L^3} \int k^2 P_r(x)\Pi_{rq}(xk)dk - \frac{G}{L^3} \int k^2 Q_r(x)\Delta_{rq}(xk)dk \tag{36}$$

where

$$\Gamma_{rq}(xk) = \int d\omega u_q \frac{\partial f_0}{\partial \epsilon} G_r \tag{37}$$

$$\Lambda_{rq}(xk) = \int d\omega u_q \frac{\partial f_0}{\partial \epsilon} \epsilon J_r \tag{38}$$

$$\Pi_{rq}(xk) = \int d\omega u_q \frac{\partial f_0}{\partial \epsilon} \epsilon G_r \tag{39}$$

$$\Delta_{rq}(xk) = \int d\omega u_q \frac{\partial f_0}{\partial \epsilon} \epsilon^2 J_r \tag{40}$$

and G is the weight attributed to an energy level. These equations are equivalent to (8) and (9) where

$$K_{rq}^{(1)} = -\frac{G}{L^3}\int k^2\Gamma_{rq}(xk)dk \tag{41}$$

$$K_{rq}^{(2)} = -\frac{G}{L^3}\int k^2\Lambda_{rq}(xk)dk \tag{42}$$

$$K_{rq}^{(3)} = -\frac{G}{L^3}\int k^2\Pi_{rq}(xk)dk \tag{43}$$

$$K_{rq}^{(4)} = -\frac{G}{L^3}\int k^2\Delta_{rq}(xk)dk. \tag{44}$$

Introducing the values of G_r and J_r from (29) and (30) into the four tensors Γ, Λ, Π and Δ one finds readily that the coefficients $K_{rq}^{(2)}$ and $K_{rq}^{(3)}$ are not symmetrical in their indices unless the conditions described in note 4 are fulfilled. Therefore these coefficients are, in general, unsymmetrical. But the reciprocal relation

$$K_{rq}^{(2)} = K_{qr}^{(3)} \tag{10}$$

does exist, for

$$\begin{aligned} K_{rq}^{(2)} = &-\frac{G}{L^3}\int k^2dk\int d\omega\frac{\partial f_0}{\partial\epsilon}u_qu_r\epsilon\frac{f_0^2e^{\epsilon/KT}k^2}{H(ka)} \\ &-\frac{G}{L^3}\int dk\int d\omega\int dk'\int d\omega'k^2k'^2u_qu_r' \\ &\cdot\frac{\partial f_0}{\partial\epsilon}\frac{f_0'^2e^{\epsilon'/KT}\epsilon'}{(H(k'a')H(ka))^{1/2}}S(xkk'aa') \end{aligned} \tag{45}$$

$$\begin{aligned} K_{qr}^{(3)} = &-\frac{G}{L^3}\int k^2dk\int d\omega\frac{\partial f_0}{\partial\epsilon}u_ru_q\epsilon\frac{f_0^2e^{\epsilon/KT}k^2}{H(ka)} \\ &-\frac{G}{L^3}\int dk\int d\omega\int dk'\int d\omega'k^2k'^2u_ru_q' \\ &\cdot\frac{\partial f_0}{\partial\epsilon}\frac{f_0'^2e^{\epsilon'/KT}\epsilon}{(H(k'a')H(ka))^{1/2}}S(xkk'aa'). \end{aligned} \tag{46}$$

Since $S(xkk'aa')$ and $(H(k'a')H(ka)^{1/2}$ are symmetrical in primed and unprimed variables, and

$$\frac{\partial f_0}{\partial\epsilon} = -\frac{f_0^2}{AKT}e^{\epsilon/KT}$$

these expressions are equal, for primed and unprimed quantities may be interchanged in the second term of either expression without changing its value.

5. The Kelvin Equations

Following Ehrenfest and Rutgers one may write the current equations in the form

$$i_s = A_{rs}eF_r + B_s \tag{47}$$

$$w_q = C_{rq}eF_r + D_q \tag{48}$$

where

$$A_{rs} = eK_{rs}^{(1)} \tag{49}$$

$$B_s = -eK_{rs}^{(1)}\frac{KT}{A}\frac{\partial A}{\partial x_r} - \frac{eK_{rs}^{(2)}}{T}\frac{\partial T}{\partial x_r} \tag{50}$$

$$C_{rq} = K_{rq}^{(3)} \tag{51}$$

$$D_q = -K_{rq}^{(3)}\frac{KT}{A}\frac{\partial A}{\partial x_r} - \frac{K_{rq}^{(4)}}{T}\frac{\partial T}{\partial x_r}. \tag{52}$$

The Kelvin relations for the reversible heat development and the thermo-electric force are obtained from these equations and a third equation giving the total heat development Ω:

$$\Omega = F_q i_q - \frac{\partial w_p}{\partial x_p}. \tag{53}$$

One obtains for the reversible part χ of the total heat developed the expression

$$\chi = -i_q B_s \frac{a_{qs}}{e} - \frac{\partial}{\partial x_p}(a_{qs}i_s C_{qp}) \tag{54}$$

and for the thermo-electric force F_q:

$$F_q = -\frac{B_s}{e}a_{qs} \tag{55}$$

where a_{qs} is a tensor which is the reciprocal of the tensor $eK_{qs}^{(1)}$ and is defined by the equation:

$$a_{qs}K_{rs}^{(1)} = \frac{\delta_{qr}}{e}. \tag{56}$$

The coefficients $K_{qs}^{(1)}$ and $K_{qs}^{(4)}$ unlike the coefficients $K_{qs}^{(2)}$ and $K_{qs}^{(3)}$ are always symmetrical. Therefore

$$a_{qs} = a_{sq}. \tag{57}$$

Introducing the expression for B_s, the general reciprocal relation (10), and Eq. (57) into Eqs. (54) and (55), one obtains the Kelvin equations:

$$\frac{\chi(x_1x_2x_3)}{T} = \frac{\partial}{\partial x_p}(i_s S_{sp}) \tag{58}$$

$$F_s = \frac{\partial R}{\partial x_s} - S_{ps} \frac{\partial T}{\partial x_p} \tag{59}$$

where

$$S_{sp} = K\left(\frac{S_{sp}}{e} \log A - a_{qr} K^{(3)}_{qp} \frac{1}{KT}\right) \tag{60}$$

$$R = \frac{KT}{e} \log A\,. \tag{61}$$

These equations are equivalent to those originally obtained by Lord Kelvin on the basis of thermo-dynamic reasoning. They have now been derived kinetically using only the assumption of detailed balancing. The essential role of this principle has been to provide the necessary symmetry in the integral equation which describes the distribution function of the electrons, on the basis of which a solution, also having certain essential symmetry characteristics, is possible. These characteristics have served to establish the symmetry of the tensor a_{qs} and the existence of important reciprocal relations between the current equations. The Kelvin relations depend essentially on these conditions.

I wish to express my gratitude to Professor G. E. Uhlenbeck for suggesting this problem.

Note added for correction: The index r of equations (17), (18), and (19) is not a dummy index. These developments are not strictly true unless the energy is separable in three functions, which may be different, of the three quantum numbers individually.

THE HALL EFFECT IN SOLID MERCURY

By James T. Serduke and Thomas F. Fisher
Union College

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Abstract

The Hall effect in solid mercury has been studied by several investigators but with uncertain or negative results. The authors have studied the Hall effect in solid mercury obtaining the mercury in strips 14 cm long, 2 cm wide and of various thicknesses down to 0.006 cm. The Hall effect is found to be independent of field strength, current density and thickness of specimen. The average value of the Hall constant R obtained is -0.000784. The longitudinal effect, if present, was not large enough to be well measured.

VARIOUS investigators have studied the Hall effect in mercury, especially in the liquid form. In the solid form Fenninger[1] in 1914 found the Hall constant, if present, is not in excess of 0.000011. The scarcity of previous work by other investigators on mercury and the uncertainty of the results led the present authors to the study of the Hall effect in solid mercury.

Apparatus and Procedure

The mercury was contained in a mold consisting of two ground plates of glass with a mica spacer between them, which was of the thickness desired for the mercury strip. Great precaution was taken in selecting mica of good quality and splitting it to a uniform thickness.

In the mica spacer there was cut an opening fourteen centimeters long and two centimeters wide, as shown in dotted lines in Fig. 1. On a line at right angles to the long axis of the opening were cut narrow slots about one half millimeter wide and four millimeters long, leading to holes A, B, C, D in the top glass plate. The holes A, B, C, formed the transverse terminals for measuring the Hall e.m.f. Holes A and D formed the terminals for measuring the longitudinal effect, i.e., the change in resistance due to the magnetic field.

Glass tubes about 0.6 cm in diameter and 10 cm long were mounted in the holes mentioned above as well as in similar holes E and F, which latter were used as leads for the primary current. The entire assembly was clamped onto a thick copper plate between two troughs arranged for holding a mixture of ether and solid carbon dioxide.

Triply distilled mercury was poured into one of the glass tubes. After sufficient pressure was built up the mercury flowed into the air space between the glass plates, filled every part of the mold and flowed out through the narrow contact slots up into the other glass tubes. If both top and bottom glass plates were perfectly clean there were no holes in the mercury strip even

[1] W. N. Fenninger, Phil. Mag. (6) **27**, 109 (1914).

though very thin mica spacers were used. The slightest trace of dirt or moisture would cause holes in the mercury strip. There was no tendency of the mercury to flow between the glass plates and the mica spacer if everything was clamped tightly.

The next step was to freeze the mercury. A mixture of solid carbon dioxide and ether was placed in troughs on either side of the mould. The copper plate conducted the heat away from the mercury strip and the mercury froze solid in a few minutes.

The glass tubes were now removed from the holes in the top plate. The mercury in these holes was frozen and the removal of the glass tubes left good contacts for the various lead wires. The mercury at this temperature be-

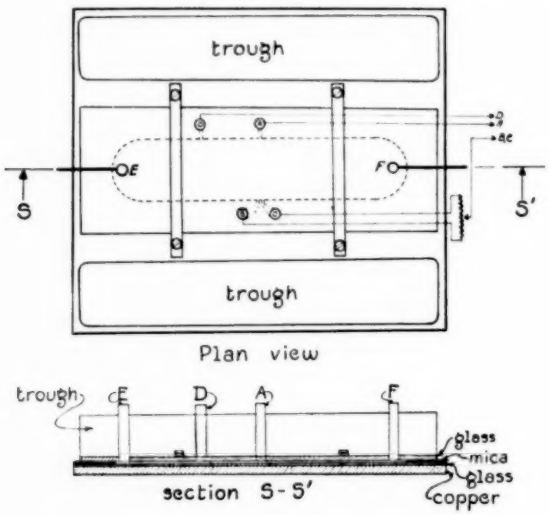

Fig. 1. Arrangement for freezing mercury strips.

haved much like solder and the lead wires were 'soldered' to the contacts, the 'soldering iron' being a screw driver heated by holding it in the hand.

The complete assembly with all leads attached was placed between the poles of an electromagnet (pole faces 5 cm in diameter), centered accurately and braced.

By careful location of the side terminals practically no transverse potential difference would be present for liquid mercury in zero field. Upon solidification, however, this potential difference was quite large compared to the Hall e.m.f. and in a wholly erratic manner for different freezings. This was probably determined by the orientation which the mercury crystal or crystals took up. It was desirable to have this "bias" quite small and this was obtained by a method suggested by Kolacek[2] with a potentiometer arrangement across two terminals B, C, about 1.5 millimeters apart.

The measurements of the Hall e.m.f. as well as the potential drop along

[2] Kolacek, Electrina a Magnetismus, Prag p. 246 (1904); Ann. d. Physik (4) **39**, 1491 (1912).

the specimen between terminals A and D were made on a Wolff potentiometer with a galvanometer of sensitivity 100 mm per microvolt.

The potential across the transverse leads was measured, while the current through the specimen was kept constant: (1) without the field; (2) with the field in one direction; (3) with the field removed; (4) with the field opposite to that in 2; (5) with the field removed.

These five steps formed one cycle of measurements for every desired flux density and current in the strip. The change in strength of the field was measured for each step.

The temperature of the mercury strip was measured by means of a thermocouple. If sufficient time was allowed for the apparatus to reach the equilibrium conditions and the troughs were kept full of ether and solid carbon dioxide, the temperature was found to be fairly constant at about $-60°$C. The variation of the temperature during an experiment was within one degree centigrade.

The thermal e.m.f. in the transverse leads was between 3 and 5 microvolts, and there was no detectable change of it during a run.

The accuracy of determination of the Hall constant is limited chiefly by the accuracy with which the thickness of the mica spacer could be measured. For the thin spacers used the measurements could be relied upon to within about 10 percent only.

Experimental Results

While Fenninger's[1] article does not indicate the sign of the small Hall effect he observed in solid mercury the present experiments show definitely a negative effect and the average Hall coefficient obtained is -0.00078 ± 10 percent, i.e., over 71 times larger than the value announced by him.

Table I. *Data for a typical run on solid mercury.*

Thickness of a specimen (cm)	Current in specimen (amp.)	Flux density B	Potential in transverse leads A–B, C (microvolts)	Hall e.m.f. (microvolts)	Hall constant	Average value of Hall constant R
0.010	13.12	0	35.9	14.7	0.000773	0.000788
0.010	13.12	+14500	50.6			
0.010	13.12	0	35.9	15.3	0.000804	
0.010	13.12	−14500	20.6			
0.010	13.12	0	36.0			

The data for a typical run on solid mercury are shown in Table I for a strip 0.010 cm thick, primary current of 13.12 amperes, from which it will be seen that the quantities to be measured are very definite and far above the limits of sensitivity of the galvanometer system. It is not understood, therefore, why Fenninger should have found such small and uncertain effects.

The curves in Fig. 2 and Fig. 3 show that the Hall coefficient R is independent of the magnetic field and the current through the specimen. A single strip was used for the data of Fig. 2 and therefore does not show uncertainty

in determination of thickness. The same remarks hold for Fig. 3. Each point on these curves is the average of four sets of readings such as shown in Table I.

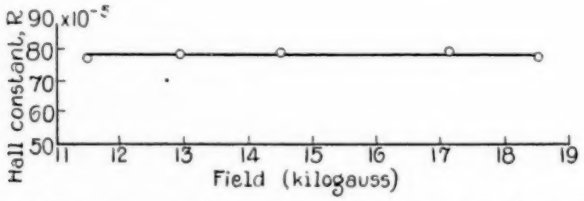

Fig. 2. Hall constant of solid mercury as a function of field strength.

Fig. 4 shows the Hall constant as a function of thickness. While the points do not lie on a straight line it is thought that this is due to the difficulties in

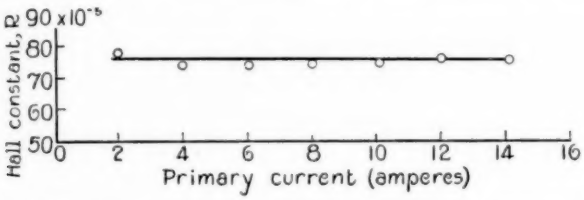

Fig. 3. Hall constant of solid mercury as a function of primary current.

measuring the thickness and that one is justified in concluding that the Hall constant in solid mercury is independent of thickness.

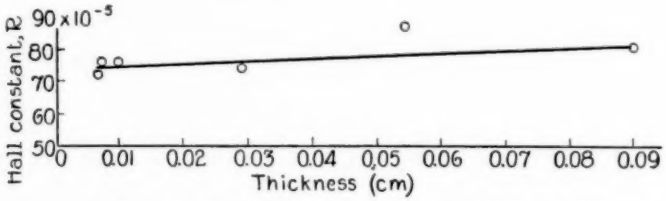

Fig. 4. Hall constant of solid mercury as a function of thickness.

The change in resistance in solid mercury due to magnetic field was not large enough to be well detected.

In conclusion the writers wish to express their gratitude to Professor P. I. Wold for the help and encouragement, which he freely gave to this investigation, which is part of a larger program on measurements of Hall effects being carried on by the Physics Department at Union College.

ON THE BEHAVIOR OF NON-STATIC MODELS OF THE UNIVERSE WHEN THE COSMOLOGICAL TERM IS OMITTED

By Richard C. Tolman and Morgan Ward
California Institute of Technology, Pasadena, California

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Abstract

If the cosmological term in the equations of relativistic mechanics is set equal to zero, it has been shown by Einstein that a non-static model of the universe filled with a homogeneous distribution of incoherent matter would expand to a maximum volume and then start contracting. This, however, is a very special model of the universe filled with a highly simplified fluid, and subjected to changes which can be shown to be thermodynamically reversible; and it has recently been pointed out by one of the present authors that we can also expect a similar expansion to a maximum volume with much more general models of the universe allowing irreversible as well as reversible changes in the fluid filling the model. The present article gives a somewhat detailed analysis of the behavior of a wide class of non-static models of the universe when the cosmological term is set equal to zero, and shows that we may expect a continued succession of expansions and contractions without reference to the reversible or irreversible nature of the processes taking place in the fluid filling the model. The bearings of this finding on the problems of relativistic thermodynamics, which have already been treated by one of the present authors, are again noted.

§ 1. *Introduction.* Einstein's original equations connecting the distribution of matter and energy with the space-time metric of general relativity can be written in the form

$$-8\pi T_{\mu\nu} = G_{\mu\nu} - \tfrac{1}{2}G g_{\mu\nu} \tag{1}$$

where $T_{\mu\nu}$ is the energy-momentum tensor, $G_{\mu\nu}$ is the contracted Riemann-Christoffel tensor, and $g_{\mu\nu}$ the fundamental metrical tensor. The choice of these equations as a starting point for relativistic mechanics has considerable justification. In empty space, they reduce to

$$G_{\mu\nu} = 0 \tag{2}$$

which has the support provided by the three well-known crucial tests of the general theory of relativity. In weak static gravitational fields, only one of the ten equations, that with $\mu=\nu=4$, is of importance and this can then be shown to reduce to Poisson's equation

$$4\pi\rho = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} \tag{3}$$

where ρ is the density of matter and ψ the ordinary Newtonian gravitational potential. And finally, the energy-momentum tensor $T_{\mu\nu}$ is a quantity whose divergence we wish to have equal to zero on physical grounds while the

combination on the right-hand side of (1) is a quantity whose divergence is known to be identically equal to zero.

As is well-known the original equations given above were later modified by Einstein's addition of the so-called cosmological term to read

$$-8\pi T_{\mu\nu} = G_{\mu\nu} - \tfrac{1}{2}Gg_{\mu\nu} + \Lambda g_{\mu\nu} \tag{4}$$

where the cosmological constant Λ is a quantity independent of the spatial and temporal coordinates, which would have to be regarded as a new fundamental constant of nature.

At the time the reason for making such a change appeared to be twofold. In the first place, by adding the cosmological term there was obtained the most general possible function, of the gravitational potentials $g_{\mu\nu}$ and their first and second differential coefficients, the divergence of which is identically equal to zero. In the second place, without the cosmological term it was impossible to construct a static model of the universe containing a finite density of matter; but by adding the cosmological term it became possible to obtain Einstein's well known static model for the universe, with reasonable values for the density of matter and radius of the model, and no disagreement with the three observational tests of the theory, provided Λ was taken as a small positive quantity.

More recently, however, the arguments in favor of changing from the original form of the equations as given by (1) have seemed less strong. In the first place, we know that Λ must in any case be a very small quantity in order to agree with the three crucial tests of the theory of relativity, and we should certainly prefer to take it equal to zero merely in the interests of simplicity and definiteness. In the second place, if we do not set Λ equal to zero, we have to inquire into the significance and magnitude of this new fundamental constant of nature, and the results of such inquiry have so far not seemed very satisfactory. Finally, it now appears evident, both from theoretical and observational points of view,[1] that non-static models of the universe are to be preferred to static models, and it is entirely possible to construct satisfactory non-static models of the universe without introducing the cosmological term, a fact that has recently been specially pointed out and emphasized by Einstein himself.[2]

For these reasons it becomes a matter of some interest to consider the consequences of omitting the cosmological term from the equations of relativistic mechanics, even though in the interests of generality we must continue to keep in mind the possibility that Λ may not be exactly equal to zero.

§2. *Purpose of the Present Article.* The purpose of the present article is to consider the general behavior of non-static models of the universe, setting

[1] On the theoretical side, as pointed out by Tolman, Proc. Nat. Acad. **16,** 320 (1930), we cannot have a static universe if matter is changing over into radiation, and as pointed out by Eddington, Monthly Notices R.A.S. **90,** 668 (1930), we cannot regard the Einstein static universe as stable. On the observational side, the red shift in the light from the extra-galactic nebulae indicates a non-static universe as first appreciated by Lemaitre, Ann. Societe Sci. Bruxelles **47,** Series A, 49 (1927).

[2] Einstein, Berl. Ber. (1931), p. 235.

the cosmological term equal to zero, and making only very general assumptions as to the nature of the fluid which fills the model, and as to the nature of the processes which occur in this fluid as the model expands or contracts.

In the article of Einstein referred to above, it was shown that on setting Λ equal to zero we must expect a non-static model of the universe, filled with incoherent matter exerting no pressure, to expand to a maximum volume and then to start contracting. This, however, was a very special model of the universe, filled with a highly simplified fluid, and subjected only to changes which can be shown to be thermodynamically reversible,[3] and it might be questioned whether we could expect a similar behavior in the case of less simple fluids and models in which irreversible processes might take place. Nevertheless, it has been pointed out in a recent article by one of us[4] that we can also expect such expansion to a maximum followed by contraction in the case of any model of the universe filled with a homogeneous distribution of fluid exerting a positive pressure, provided we set the cosmological term equal to zero. In the present article this behavior will be considered in more detail.

In the next section, §3, we shall give those mechanical equations governing the behavior of non-static universes which will be needed later. In §4, we shall then prove for any such non-static model of the universe, filled with a fluid which could exert only positive pressures, and having initially a finite volume and finite rate of expansion, that there would be a finite upper boundary beyond which the volume could not expand. Continuing in §5, we shall then show that the model would reach its maximum upper volume in a finite time and would then start contracting. And in §6, we shall show that the equations would thereafter require the contraction to continue to zero volume which would also be reached within a finite time. In §7, we shall then discuss this mathematical conclusion that the model would contract down to the exceptional point of zero volume, and show from a physical point of view that we might expect contraction to the lower limit to be followed by a renewed expansion. Finally in §8, we shall make some remarks concerning the possible application of these conclusions as to the behavior of highly idealized models, in interpreting the behavior of the actual universe.

§3. *The Mechanics of the Non-Static Universe.* An expression for the line element for a non-static model of the universe filled with a homogeneous distribution of fluid with properties which are independent of position but dependent on the time, can be derived[5] and written in the form

$$ds^2 = -\frac{e^{g(t)}}{[1 + r^2/4R^2]^2}(dr^2 + r^2 d\theta^2 + r^2 \sin^2\theta d\phi^2) + dt^2 \qquad (5)$$

where r, θ and ϕ are the spatial coordinates, t is the time coordinate, R is a constant, and the dependence of the line element on the time is given by the exponent $g(t)$.

[3] Tolman, Phys. Rev. **38**, 1758 (1931). See 9.
[4] Tolman, Phys. Rev. **39**, 320 (1932).
[5] Tolman, Proc. Nat. Acad. **16**, 320 (1930).

For the proper pressure p_0 and proper macroscopic density ρ_{00} corresponding to this line element we can write in accordance with the principles of relativistic mechanics[6]

$$8\pi p_0 = -\frac{1}{R^2} e^{-g} - \tfrac{3}{4}\dot{g}^2 + \Lambda \tag{6a}$$

$$8\pi \rho_{00} = \frac{3}{R^2} e^{-g} + \tfrac{3}{4}\dot{g}^2 - \Lambda \tag{7a}$$

provided we retain the cosmological term, or

$$8\pi p_0 = -\frac{1}{R^2} e^{-g} - \ddot{g} - \tfrac{3}{4}\dot{g}^2 \tag{6b}$$

$$8\pi \rho_{00} = \frac{3}{R^2} e^{-g} + \tfrac{3}{4}\dot{g}^2 \tag{7b}$$

if we set the cosmological term equal to zero, as is of prime interest for the present article. The pressure and density are independent of position and dependent as shown on the exponent $g(t)$ and its time derivatives $\dot{g}$ and $\ddot{g}$.

With the above choice of coordinates particles which are at rest with respect to r, θ and ϕ will not be subject to gravitational acceleration, so that we can regard the fluid as macroscopically at rest in these coordinates. As g changes with the time, however, the proper volume

$$\delta V_0 = \frac{r^2 \sin\theta e^{3g/2}}{\left[1 + r^2/4R^2\right]^3} \delta r \delta\theta \delta\phi \tag{8}$$

associated with a small range in coordinates $\delta r \delta\theta \delta\phi$, and the total integrated proper volume of the model[7]

$$V_0 = \pi^2 R^3 e^{3g/2} \tag{8a}$$

will change with the time. Hence we can describe the changes that take place in such a universe, as g increases or decreases, as expansions or contractions in the proper volume of the elements of fluid which fill the model, and in the total proper volume of the model.

Furthermore, in accordance with the expressions for pressure and density we can easily obtain the relation[8]

$$\frac{d}{dt}(\rho_{00}\delta V_0) + p_0 \frac{d}{dt}(\delta V_0) = 0 \tag{9}$$

which shows that the change in the energy content of any given small element of the fluid, as measured by a local observer using proper coordinates, will be found equal to the negative of the work performed on the surroundings.

[6] Reference 5, Eqs. 34.

[7] Tolman, Phys. Rev. **37,** 1652 (1931). Eq. (28).

[8] Tolman, Proc. Nat. Acad. **16,** 409 (1930). Eq. (4).

§4. *The Upper Boundary of Expansion.* Let us now consider such a model of the universe filled with a mixture of matter and radiation which might exert a positive pressure

$$p_0 \geqq 0 \tag{10}$$

but cannot withstand tension. And at some initial time $t=0$ let the model have a finite volume and finite rate of expansion corresponding to

$$g = g_0 \text{ and } \dot{g} = \dot{g}_0 \tag{11}$$

where g_0 is finite and $\dot{g}_0$ is finite and positive. We shall first show, with $\Lambda=0$, that there will be a finite upper volume beyond which the expansion cannot go, that is a finite upper boundary for the quantity g.

Combining equation (6b) with the inequality (10), we can write in general

$$\ddot{g} + \tfrac{3}{4}\dot{g}^2 + \frac{1}{R^2}e^{-g} \leqq 0. \tag{12}$$

Furthermore, since $\dot{g}$ will be positive as long as expansion continues we can multiply (12) by the positive quantity $2e^{3g/2}\dot{g}$ and write

$$2e^{3g/2}\ddot{g}\dot{g} + \frac{3}{2}e^{3g/2}\dot{g}^3 + \frac{2}{R^2}e^{g/2}\dot{g} \leqq 0 \tag{13}$$

or

$$\frac{d}{dt}(e^{3g/2}\dot{g}^2) + \frac{4}{R^2}\frac{d}{dt}(e^{g/2}) \leqq 0 \tag{14}$$

as an expression which will continue to hold as long as g continues to increase.

Integrating (14) between $t=0$ and any later time of interest $t=t$, and substituting the values for g and $\dot{g}$ at time $t=0$ as given by (11), we obtain

$$e^{3g/2}\dot{g}^2 + \frac{4}{R^2}e^{g/2} \leqq e^{3g_0/2}\dot{g}_0^2 + \frac{4}{R^2}e^{g_0/2} \tag{15}$$

or, taking the constant R as real for the models in which we shall be interested,

$$e^{g/2} \leqq \frac{R^2}{4}e^{3g_0/2}\dot{g}_0^2 + e^{g_0/2} - \frac{R^2}{4}e^{3g/2}\dot{g}^2 \tag{16}$$

as an expression which will hold as long as g continues to increase. Since g_0 and $\dot{g}_0$ are, however, finite by hypothesis this shows that there is an upper finite boundary say γ which g cannot surpass. So that we can necessarily write

$$g \leqq \gamma \tag{17}$$

where γ is finite.

§5. *Time Necessary to Reach the Maximum.* From the inequality (17) we can then evidently write

$$-\frac{1}{R^2}e^{-g} \leqq -\frac{1}{R^2}e^{-\gamma} \tag{18}$$

and combining this with (12) we obtain

$$\ddot{g} \leqq -\frac{1}{R^2}e^{-\gamma} - \tfrac{3}{4}\dot{g}^2 \tag{19}$$

or

$$\frac{d\dot{g}}{dt} \leqq -\frac{1}{R^2}e^{-\gamma}. \tag{20}$$

And integrating this between $t=0$ and any later time of interest $t=t$, we obtain

$$\dot{g} \leqq \dot{g}_0 - \frac{1}{R^2}e^{-\gamma}t \tag{21}$$

where $\dot{g}_0$ is the rate of increase in g at $t=0$.

In accordance with this expression, however, noting from (11) that $\dot{g}_0$ is positive, we see that at a finite time

$$t \leqq R^2 e^{\gamma} g_0 \tag{22}$$

$\dot{g}$ will become equal to zero, g will pass through a maximum, and the volume will start to decrease.

§6. *Time Necessary to Reach Zero Volume.* It will also be of interest to consider the behavior of the model after passing through its maximum volume. Since $\dot{g}$ will then evidently be negative, we may this time multiply (12) by the negative quantity $2e^{3\vartheta/2}\dot{g}$, and integrating as in §4, obtain in correspondence with (15)

$$e^{3\vartheta/2}\dot{g}^2 + \frac{4}{R^2}e^{\vartheta/2} \geqq e^{3\vartheta_m/2}\dot{g}_m{}^2 + \frac{4}{R^2}e^{\vartheta_m/2} \tag{23}$$

where g_m and $\dot{g}_m$ are the values of the quantities indicated on passing through the maximum point at the time $t=t_m$. Since, however, the velocity will be zero when the model passes through its maximum volume, we may substitute

$$\dot{g}_m = 0 \tag{24}$$

and rewrite (23) in the form

$$e^{3\vartheta/2}\dot{g}^2 \geqq \frac{4}{R^2}(e^{\vartheta_m/2} - e^{\vartheta/2}) \tag{25}$$

and with $\dot{g}$ negative this gives us

$$e^{3\vartheta/4}\frac{dg}{dt} \leqq -\frac{2}{R}(e^{\vartheta_m/2} - e^{\vartheta/2})^{1/2} \tag{26}$$

provided we take the constant R not only as real but positive, which will be the case for a closed model with the positive "radius" $Re^{\vartheta/2}$.

Expression (26), however, can easily be integrated between $t=t_m$ and any later time of interest $t=t$ to give

$$-\frac{e^{g/4}}{2}(e^{g_m/2}-e^{g/2})^{1/2}+\frac{e^{g_m/2}}{2}\sin^{-1}\frac{e^{g/4}}{e^{g_m/4}}-\frac{\pi}{4}e^{g_m/2}\leqq-\frac{(t-t_m)}{2R} \tag{27}$$

or on rearranging

$$(t-t_m)\leqq R\left[e^{g/4}(e^{g_m/2}-e^{g/2})^{1/2}-e^{g_m/2}\sin^{-1}\frac{e^{g/4}}{e^{g_m/4}}+\frac{\pi}{2}e^{g_m/2}\right]. \tag{28}$$

And in accordance with this result, it is evident that $e^{g/4}$ will reach the value zero or g the value minus infinity at a finite time after the maximum

$$(t-t_m)\leqq\frac{\pi}{2}Re^{g_m/2}. \tag{29}$$

We have thus shown not only that the model, starting with a finite volume and finite rate of expansion, would reach a finite maximum volume within a finite time, but continuing beyond the maximum would go on down to zero volume within a finite time later. In addition it will be noted, by comparing equations (6a) and (6b) and examining the method of analysis which has been employed, that these results would also hold if the cosmological constant Λ were taken as a negative quantity, as well as for the case which we have treated with the cosmological term set equal to zero.

§7. *Behavior of the Model on Reaching Zero Volume.* As a result of the preceding section we have seen that our equations lead to the conclusion that the proper volume of the model would decrease to the value zero within a finite time after passing the maximum. We must now inquire into the physical significance of this result, and into the further behavior of the model after reaching this exceptional point.

In accordance with the inequality (26) we may write

$$\dot{g}\leqq-\frac{2}{Re^{3g/4}}(e^{g_m/2}-e^{g/2})^{1/2} \tag{30}$$

as an expression which holds at any time after passage of the maximum, so that on reaching zero volume with $g=-\infty$ we shall have

$$\dot{g}=-\infty. \tag{31}$$

Furthermore, in accordance with our general expression (12) we can write

$$\ddot{g}\leqq-\frac{1}{R^2}e^{-g}-\tfrac{3}{4}\dot{g}^2 \tag{32}$$

so that we shall also have

$$\ddot{g}=-\infty \tag{33}$$

on reaching zero volume. The exceptional point $g=-\infty$ is thus reached with the velocity $\dot{g}$ and the acceleration $\ddot{g}$ both equal to minus infinity.

The conditions for an analytical minimum are thus unsatisfied and the analysis fails to describe the passage through the exceptional point of zero

volume. From a mathematical point of view, however, it is evident that our differential equations of motion (6b, 7b) can be satisfied if we have a renewed expansion taking place at this point, and from a physical point of view as previously emphasized by one of us[9] it is evident that contraction to zero volume could only be followed by renewed expansion. Furthermore, as noted in a similar connection by Einstein,[10] it is possible that the idealization upon which our considerations have been based should be regarded as failing in the neighborhood of zero volume[11] so that the analysis fails to give a correct description of the behavior at the lower limit of volume. It hence appears reasonable to conclude for models of the kind we are discussing that the contraction to zero volume or more generally to the lower limit of volume would result in a sudden reversal in the direction of the velocity $\dot{g}$, followed by a renewed expansion of similar character to the previous one.

§8. *Conclusion.* The main results of the foregoing analysis may now be summarized and a few remarks made concerning their significance.

It has previously been shown that the line element for any non-static model of the universe containing a uniform distribution of fluid can be written in the general form

$$ds^2 = -\frac{e^{g(t)}}{[1 + r^2/4R^2]^2}(dr^2 + r^2 d\theta^2 + r^2 \sin^2\theta d\phi^2) + dt^2 \qquad (34)$$

where R is a constant and the dependence of the line element on the time is given by the exponent $g(t)$. The "radius" for such a model is $Re^{g/2}$, and the changes that take place in the model, as g increases or decreases, can be described as expansions or contractions in the proper volume of the elements of the material filling the model, and in the total proper volume of the model as a whole.

Let us now consider the special case of a "closed" model with R real[12] and positive, filled with a perfect fluid which could not withstand tension, and having at some initial time a finite volume and finite rate of expansion. Applying the equations of relativistic mechanics with the cosmological term omitted, it has then been rigorously shown that such a model would expand to a finite maximum volume which would be reached within a finite time, and would then contract to zero volume which would also be reached within a finite time later. Furthermore, although the mathematical analysis fails to carry us through the exceptional point of zero volume, it has been shown plausible on physical grounds to expect that contraction to the lower limit would be followed by renewed expansion, thus leading to a continued succession of somewhat similar expansions and contractions.

[9] Tolman, Phys. Rev. **38**, 1758 (1931). See §7.

[10] Reference 2.

[11] The assumptions that the material filling the model has a perfectly homogeneous distribution, and that this material is a perfect fluid incapable of shearing stresses, may fail at very small volumes.

[12] It should be emphasized that these conclusions apply to "closed" models with R real. The theoretical possibility for "hyperbolic" models with R imaginary has recently been pointed out by Heckmann, Göttingen Nachrichten II, 126 (1931).

This result applies of course in the first instance only to the class of simplified cosmological models that we have considered. Nevertheless, in view of the fairly general nature of the assumptions that were necessary, the result may at least be taken as indicating a possibility that the actual universe or parts thereof might also exhibit such a continued succession of expansions and contractions.

Furthermore, it may again be pointed out, as was emphasized in a previous article,[13] that this result has been obtained solely by applying the principles of relativistic mechanics, without the necessity for any assumption as to the thermodynamic nature of the processes which take place in the fluid in the model as a consequence of the expansion and contraction. We are hence led to the conclusion that the continued series of expansions and contractions would recur even though the processes taking place in the fluid might be thermodynamically irreversible in character.[14]

This latter conclusion is of particular interest since the classical thermodynamics would have led us to expect that the continued occurrence of irreversible processes would result in a condition of maximum entropy where further change would be impossible. As shown in detail in the article mentioned, however, relativistic thermodynamics would permit a continued succession of irreversible expansions and contractions without the entropy ever reaching an unsurpassable maximum.

[13] Reference 4.

[14] If the processes taking place in the fluid are thermodynamically reversible we may expect a series of identical expansions and contractions as previously studied in detail (Ref. 9) When the processes are thermodynamically irreversible, however, we may expect a series of non-identical expansions and contractions of gradually increasing amplitude as studied in the article mentioned. (Ref. 4).

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Diamagnetic Susceptibility of the Rare Gas Atoms According to Slater's Method

Recently Biswas[1] has communicated a letter having the above title in which he gives he calculated atomic diamagnetic susceptibilities of krypton, xenon, and radon. His results are vitiated (1) by a misinterpretation of Slater's screening rules[2] and (2) by arithmetical inaccuracies. In determining the effective nuclear charge one is concerned not with the *order* in which electron groups are completed but with the *completed* groups which are present. Therefore, although most certainly the eight electrons of the 5*s*, *p* groups are added before the fourteen electrons of the

[1] S. C. Biswas, Phys. Rev. **38**, 1784 (1931).
[2] J. C. Slater, Phys. Rev. **36**, 57 (1930).

TABLE I.

Atom	Electron Group	$(Z-s)$			$-\Delta\chi_A\times10^6$			$-\chi_A\times10^6$		
		S.C.B.	J.C.S.	W.R.A.	S.C.B.	J.C.S.	W.R.A.	S.C.B.	J.C.S.	W.R.A.
Kr	1*s* (2)	31.8	35.7	35.7	—	—	—			
	2*s* (2)	31.855	31.85	32.95		0.05	0.04			
	2*p* (6)	31.855	31.85	31.85	0.19	0.14	0.14			
	3*s* (2)	24.7	24.75	26.85		0.33	0.28			
	3*p* (6)	24.7	24.75	24.75	1.33	1.00	1.00			
	3*d* (10)	14.8	14.85	14.85	4.61	4.61	4.61			
	4*s* (2)	8.2	8.25	10.35		6.40	4.06			
	4*p* (6)	8.2	8.25	8.25	31.75	19.20	19.20	37.88	31.73	29.33
Xe	1*s* (2)	—	53.7	53.7	—	—	—			
	2*s* (2)	51.85	49.85	51.95		0.02	0.02			
	2*p* (6)	51.85	49.85	49.85	0.07	0.06	0.06			
	3*s* (2)	42.7	42.75	44.85		0.11	0.10			
	3*p* (6)	42.7	42.75	42.75	0.45	0.34	0.34			
	3*d* (10)	32.8	32.85	32.85	0.95	0.94	0.94			
	4*s* (2)	26.2	26.25	28.35		0.63	0.54			
	4*p* (6)	26.2	26.25	26.25	2.54	1.90	1.90			
	4*d* (10)	14.8	14.85	14.85	9.89	9.87	9.87			
	5*s* (2)	8.2	8.25	10.35		8.53	5.41			
	5*p* (6)	8.2	8.25	8.25	34.94	25.60	25.60	48.84	48.00	44.78
Rn	1*s* (2)	—	85.7	85.7	—	—	—			
	2*s* (2)	81.85	81.85	83.95		0.01	0.01			
	2*p* (6)	81.85	81.85	81.85	0.03	0.02	0.02			
	3*s* (2)	74.7	74.75	76.85		0.04	0.03			
	3*p* (6)	74.7	74.75	74.75	0.15	0.11	0.11			
	3*d* (10)	65.5	64.85	64.85	0.26	0.24	0.24			
	4*s* (2)	58.2	58.25	60.35		0.13	0.12			
	4*p* (6)	58.2	58.25	58.25	0.49	0.38	0.38			
	4*d* (10)	46.8	46.85	46.85	0.99	0.99	0.99			
	4*f* (14)	27.4	35.45	35.45	4.05	2.42	2.42			
	5*s* (2)	40.2	28.35	30.45		0.72	0.63			
	5*p* (6)	40.2	28.35	28.35	1.44	2.17	2.17			
	5*d* (10)	14.8	14.85	14.85	13.17	13.19	13.19			
	6*s* (2)	10.3	8.25	10.35		10.21	6.49			
	6*p* (6)	10.3	8.25	8.25	25.98	30.63	30.63	46.56	61.26	57.43

$4f$ group, in evaluating the effective nuclear charge one must consider the screening effect produced by the $4f$ electrons on the electrons in the $5s$, p groups; but this is entirely neglected by Biswas.

In Table I are given the electron groups and, in brackets, the number of electrons in each group. $(Z-s)$ is the effective nuclear charge calculated by Biswas (S.C.B.), by a rigorous adherence to Slater's rules (J.C.S.), and by a modification of Slater's rules which I have made (W.R.A.). This modification consists in evaluating $(Z-s)$ by using Slater's screening factors for the s and p groups separately with a consequent increase of 2.1 for the $(Z-s)$ value of every s group over every p group having the same principal quantum number. This means a lowering of the diamagnetic susceptibility and values calculated for a large number of atoms and ions will be published shortly elsewhere. The values obtained by the modified method are in much better agreement with experimental results than values calculated by any of the previously known methods. The diamagnetic increments of each electron group $(-\Delta\chi_A \times 10^6)$ and the atomic diamagnetic susceptibilities $(-\chi_A \times 10^6)$ calculated by Slater's method and by the method just discussed are compared with the values given by Biswas. The agreement is not good.

W. Rogie Angus

Sir William Ramsay Laboratories
of Inorganic and Physical Chemistry,
University College,
London,
February 2, 1932.

The Shot Effect and Electrical Breakdown in Insulators

Since Schottky first discovered and interpreted the shot effect in vacuum tube circuits, the theory has been applied to a variety of problems. Now it seems evident that studies of the amplified electrical fluctuations accompanying many physical phenomena are valuable in getting a better insight into the physical processes involved. We have recently measured the fluctuations in currents through insulating materials subjected to high electric fields, and as a result have been led to certain conclusions regarding the nature of electrical breakdown in solids.

The apparatus was similar to that usually used in measurements of the shot effect, except that the coupling with the amplifier was non-inductive. A battery of dry cells was connected in series with a condenser made of a thin film of the insulating material to be tested, and with a high resistance across which the amplifier was connected. The fluctuations in the current through the insulator were thus transmitted to the amplifier and measured by the power dissipated in a thermocouple connected to the amplifier output. The amplifier was calibrated by measuring the thermal noise[1] with the battery disconnected. The principle of this calibration will be discussed in more detail later.

For most of the measurements, the insulator used was a Pyrex glass bulb 5μ thick at the thinnest part. Electrical contact was usually made inside and outside with clean mercury. After the voltage was applied, the direct current, measured directly with a galvanometer, at first decreased rapidly, but after about five minutes became rather steady, whereupon the noise measurements were made. Tests were made showing that the noise was not merely an electrode phenomenon.

The existence of the noise we have measured proves that the strength of the conduction current fluctuates; quantitative measurements determine the magnitude of the fluctuations. We express the results in terms of the number, n, of charges equal in magnitude (but not necessarily in sign) to the electronic charge, which discharge onto the electrodes together. As in similar noise measurements, the theory[2] of the shot effect enables us to derive from the results of experiment, the value of $\overline{n^2}/\bar{n}$, the average value of the square of the number divided by the average value of this number. We shall refer to this quantity simply as the group-size. The results for Pyrex glass are shown in Fig. 1.

It is interesting to consider the results in relation to the theories of breakdown by cumulative ionization. Joffé,[3] in particular, views the conducting ions as being speeded up by the field until finally they have momentum enough to loosen more ions from the lattice, resulting in increased conductivity and finally

[1] J. B. Johnson, Phys. Rev. (2) **32,** 97 (1928).

[2] T. C. Fry, Jour. Franklin Inst. **199,** 203 (1925).

[3] The Physics of Crystals, McGraw Hill, New York, 162 (1928).

breakdown. Qualitatively, our results fit in with Joffé's theory, for according to it we should expect ion groups the sizes of which would increase rapidly with voltage. But quantitatively the group-size should be about the same as the ratio of the conductivity in the field in which the group-size was measured, to the conductivity in very low fields. In Pyrex glass films 5μ thick, in a field of $2 \cdot 10^6$ volts/cm, this conductivity ratio is about 5, while our observed group-size is 10^5, quite inconsistent with Joffé's simple picture of incipient breakdown. If we retain Joffé's theory of the increase in conductivity in high fields, the average group-size is measured by the conductivity ratio (in this case a maximum of 5), and using our experimental value of $\bar{n}^2/\bar{n}$ we find that the average square of the group size is $5 \cdot 10^5$. This is just what we should expect if a few of the groups are very much larger than the others; e.g., if most of the groups have the size $n=5$, and 10^{-7} of them the size 10^6, $\bar{n}^2/\bar{n}$ has the value $2 \cdot 10^4$ and still only 2 percent of the current is carried by the larger groups.

Thus it is suggested that most of the noise which we have measured is due to a succession of discharges which are very much larger than the average. It is possible that these discharges occur in paths along which breakdown would occur at higher voltages. Support for this idea is found in the work of Inge and Walther,[4] who observed microscopic channels in glass and rock salt when a field ordinarily sufficient for breakdown was applied for a very short time. Although the channels could afterwards be observed under the microscope, their presence did not lower the breakdown strength of the material as ordinarily measured. It was only after the field was applied for longer times that these channels grew in size sufficiently to cause complete breakdown. It seems probable that the groups of charges which we have measured have passed along submicroscopic paths which at higher voltages grow into the microscopic paths observed by Inge and Walther, and finally enlarge to produce breakdown.

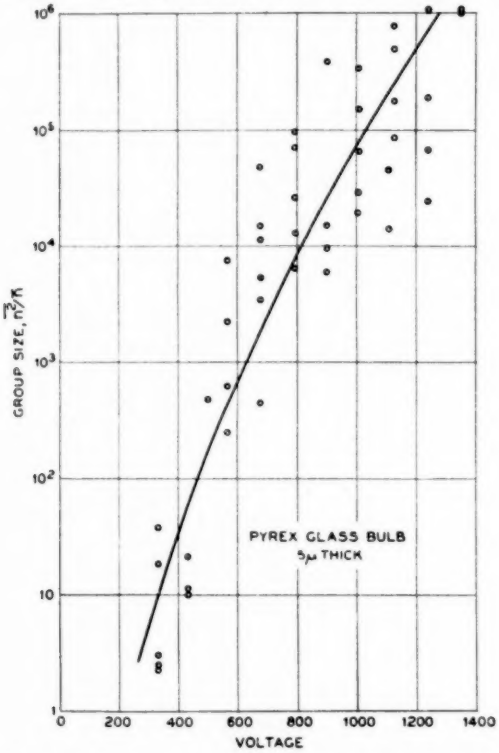

Fig. 1. Group-size as dependent upon voltage. Here n represents the number of charges, equal in magnitude to the charge of one electron, which discharge onto the electrodes together. The quantity determined by experiments on the shot effect is the ratio of the means, $\bar{n}^2/\bar{n}$.

[4] Inge and Walther, Archiv. f. Electrotech. **24,** 259 (1930).

The existence of a few groups which are much larger than the average and which carry only a small fraction of the conduction current, suggests that the carriers composing these groups are quite different from most of the carriers, and that they are electrons rather than ions. This opinion is supported by recent work of von Hippel[5] which indicates that electrical breakdown, which may be regarded as a later stage in the development of the phenomenon we have observed, is primarily an electronic phenomenon.

R. M. Bozorth
F. E. Haworth
Bell Telephone Laboratories, Inc.,
New York, N. Y.,
February 3, 1932.

[5] v. Hippel, Zeits. f. Physik **67,** 707; **68,** 309 (1931).

The Isotopic Constitution of Zinc

The constitution of zinc has been determined by a new method of analysis. The mass numbers of the isotopes of zinc are 64, 66, 68, 67, and 70 in order of relative abundance. No evidence has been secured for the existence of Zn^{65} or Zn^{69} although from Aston's[1] measurements Zn^{65} and Zn^{69} are respectively 6.5 and 2 times more abundant than Zn^{70}. This new analysis indicates that *the ions of mass numbers 65 and 69 measured by Aston were hydrides of* Zn^{64} *and* Zn^{68}. Fig. 1 is a positive contact

64 66 67 68 70

Fig. 1.

print of the mass-spectrum of zinc. Zn^{70} is clearly visible on the original plate. Fig. 2 is a densitometer record of the mass spectrum of zinc.

The apparatus used for this analysis of the isotopes of zinc may be most simply described as a combination of a source of ions, a "velocity filter" or selector, and a focussing chamber and camera. Ions of all energies up to the maximum potential applied across the discharge tube enter the first slit, (0.005 cm wide), of the velocity selector. In this region the ions are subjected to the combined action of crossed electric and magnetic fields. All ions passing through the second slit of the velocity selector have the same velocity, $v = X/H$, within narrow limits. The ions which emerge from the second slit are immediately introduced into a uniform magnetic field, and arrive normally incident to the surface of a photographic plate 180° from the second slit. The radius of curvature of the ions is proportional to the mass of the ions and a linear mass scale is secured.

The present analysis of zinc was undertaken as the available evidence indicated that the ions of mass 65 and 69 as measured by Aston were not isotopes of zinc. Dempster[2] determined the isotopes of zinc by means of his method of analysis. The ions were produced by electron impact of zinc vapor essentially free from hydrogen. Isotopes of proton numbers 64, 66, 68, and 70 were found with indications of an isotope at 67 *but no evidence for an isotope of mass 69*. Aston[3] has suggested in commenting on his analysis of germanium that "the possibility of hydrides cannot be ruled out". The germanium ions were produced from a volatile compound containing hydrogen in abundance which was released under the dissociative action of the discharge. Zinc methyl was used in the discharge tube to produce zinc ions and again large quantities of hydrogen must have been present under conditions favorable to the formation of hydrides. Barton[4] has called attention to the possibility of error in the analysis of germanium due to hydrides and has suggested less directly that Aston's analysis of zinc might be in error.

For the present analysis, the ions of zinc were secured by ionization of metallic zinc vapor from a new type of source which may prove to have a wide range of application. A zinc cathode was used in the discharge tube and for some spectra metallic zinc was also deposited by evaporation from a tungsten filament onto the walls of a cylindrical discharge tube. When a discharge is run in neon or argon, a copious supply of metallic ions is secured. This method of producing ions was discovered quite accidentally when it was noticed in examining the abundance of Ne^{21} that an intense line of mass 27 always appeared on these plates when an aluminium cathode was used. The origin of the metallic

[1] F. W. Aston, Nature **122,** 345 (1928); Proc. Roy. Soc. **A130,** 303 (1931).
[2] A.J. Dempster, Phys. Rev. **20,** 635 (1922).
[3] F. W. Aston, Nature **122,** 167 (1928).
[4] H. A. Barton, Phys. Rev. **35,** 412 (1930).

vapor has not been located precisely; the cathode becomes very hot and considerable metallic vapor is continually given off by evaporation and sputtering. Although the intensity of the ion beam is increased by allowing the walls of the discharge tubes to heat up to 200° by electron bombardment and the recombination of ions and electrons on the walls, good ion intensity can be secured with the discharge tube cool and no metal on the walls. It appears therefore that the cathode surface supplies most of the metallic vapor. So far this type of source has been used successfully for

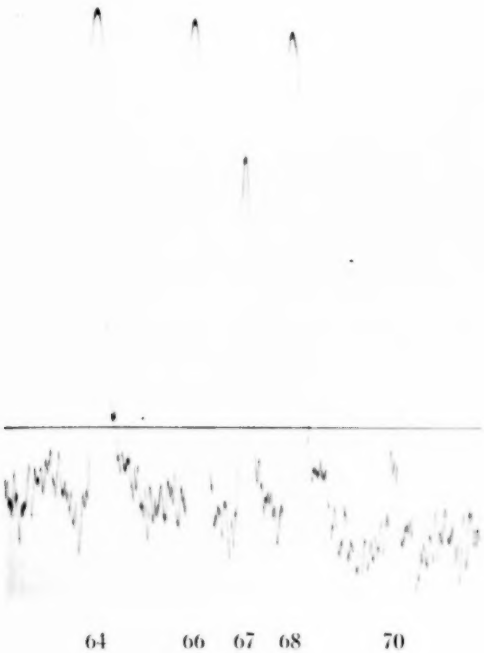

Fig. 2.

Al, Zn and Cd. It is peculiarly adapted for examining elements which form hydrides as the great affinity of ionized neon and argon for hydrogen tends to clean up any hydrogen present in the discharge tube. A "well" (filled with Se) in an aluminium cathode was a successful source of vapor for this element. The vapor pressures of Cd and Se are too great to allow the use of cathodes of these materials as the discharge tube walls become conducting too rapidly to permit a series of exposures.

A critical examination of Aston's results obtained since 1927 shows that in regard to the existence of specific isotopes only the analysis of germanium is questionable. Similarly, Aston's measurements of the relative abundance of isotopes are not in question insofar as they might be affected by the presence of hydrides except for Zn and Ge. "Consistent photometry of '*a*' group of lines on all of a very large number of plates"[5] is not a sufficient criterion to prove that hydrides are not present among those lines.

Assuming that all the isotopes of zinc form hydrides in the same ratio as Zn^{64} to $Zn^{64}H$ and no multiple hydrides are formed, the value obtained for the atomic weight of zinc from Aston's data and with the present results in view is $65.32_7 \pm 0.02$ on the chemical scale after deducting 2.2 parts in ten thousand[6] to transfer from the physical mass scale.

KENNETH T. BAINBRIDGE

Bartol Research Foundation of
The Franklin Institute,
Swarthmore, Pa.,
February 10, 1932.

[5] F. W. Aston, Proc. Roy. Soc. **130,** 305 (1931).

[6] R. T. Birge and D. H. Menzel, Phys. Rev. **37,** 1669 (1931).

BOOK REVIEWS

Science and First Principles. F. S. C. NORTHROP, xiv+299 pp. The MacMillan Company, New York, 1931. Price, $3.00.

In this book, the author applies the principles of philosophy to the modern physics in an attempt to discover what are the realities behind the mathematical statements of the physicists. To do this, he reviews the theories of nature, starting with the Greeks and ending with Einstein, examining carefully the fundamental postulates of each one, and he concludes that the physical theory of nature, as stated by Einstein in the relativity theories, is the correct one in the light of modern work, provided only there exists a referent, outside of the "atoms" themselves, which also must be a physical thing. This referent, the author contends is itself an "atom"—a macroscopic atom of finite diameter, which is a physical entity congesting and surrounding all the microscopic atoms of nature. By means of this one macroscopic atom and the many microscopic atoms, there are provided the "approximate general uniformity over macroscopic distances, and the local microscopic heterogeneity and variability" which are necessitated by the relativity and the unitary field theories. After applying his macroscopic atomic theory to quantum and wave mechanics and to thermodynamics, in each case searching out and examining the fundamental principles behind the scientific generalizations, the author then proceeds to show that his new theory is of the most general validity by applying it successfully to the living organisms and to man himself, finally ending with a chapter on the foundations of experience and knowledge.

To an organic chemist, quite bewildered by some of the interpretations of the mathematical equations of modern physics, and wondering whether or not the atoms and molecules with which he is working today will be tomorrow nothing but mathematic equations, this book comes as a great joy. Not that the chemist can understand it all—far from it—but the book does give him a hopeful inkling that, after all, there are real, physical meanings to these mathematical equations, meanings which are not so difficult to grasp as the sight of the mathematical equations had led him (and others!) to suppose.

A distinguished scientist, lecturing recently at the University of Minnesota, made the statement "In the old days, we could explain a great deal, but could not calculate very much; now, however, we can calculate much more, but can explain much less". It is the business of this book to do some explaining and to clear away some of the rubbish which today passes for scientific thinking, even in high circles. Even if the author's theory later has to be modified, he has so far done an excellent job in calling attention to inconsistencies in the use and application of the recent outstanding mathematical developments of modern science, and for this he deserves the heartfelt thanks of all scientists.

The author's range of information covers many fields, and he writes exceedingly well on all of them. The book is well printed, in readable type, and on good paper. There are very few typographical errors, and at the end there is an adequate index.

LEE IRVIN SMITH
University of Minnesota

Jahrbuch des Forschungs-Instituts der Allgemeinen Elektricitats-Gesellschaft, Volume II, 1930. 332 pp., Julius Springer, Berlin, 1931.

This volume consists of a collection of the important publications of the relatively newly organized research laboratories of the Allgemeinen Elektricitäts-Gesellschaft, Germany. These papers have all appeared in a large number of scientific and technical journals during the year 1930. They are brought together in book form under 12 groups constituting the chief activities of the research laboratory. These groups are Acoustics, Investigation of Transient Phenomena of Short Duration by means of Photography, Studies of Electrical Heating Devices, Vacuum Tube Technique, Electron Beams, Electron Physics, Atomic Physics, Atomic Chemistry, Physical Chemistry, Properties of Matter, Electro-optics and Unclassified.

The first chapter consists of a description of the research laboratories of the A.E.-G and the projects under way by C. Ramsauer. Among the collected papers there is one of general popular interest which is a beautifully written article on the reproduction and registration of music by photographic films, written by Dr. Hehlgans-Lichte. In addition there are some excellent technical papers on the photographic problems of photographic sound registration, on the acoustical radiation from membranes and on the horn loud speaker.

The article dealing with the theory and applications of Dr. Tuhn's method for photographic registration of short time phenomena is also illuminating.

Particularly notable is the collection of papers on electron beams by Brüche in which he discusses a large number of technical applications of the slower electron beams, and in particular the collection of his excellent articles in which he investigates and demonstrates phenomena of the aurora borealis by means of electron beams in magnetic fields.

Another good collection of papers is that by Rupp, giving his interesting results on electron diffraction.

Perhaps the most outstanding and complete collection of papers is that of Ramsauer and Kollath on the absorbing cross-section of molecules together with their application to the study of molecular structure by Brüche.

The book is excellently printed, well bound and profusely illustrated. The feature of particular interest is that there are collected in one volume the outstanding papers for the year of one of the most active research laboratories, classified in such a way that they are easily accessible for persons interested in the fields of activity covered by this research laboratory. In view of the wide dissemination of scientific papers on the same subject often by the same author in many journals, the idea of collecting the year's work in a single volume properly classified is a most happy one. The volume should be in all scientific libraries and would be of great value to men working in the special fields of investigation covered.

LEONARD B. LOEB
University of California

Gmelin's Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft, System Nummer 29: Strontium. Pp. 239, figs. 26 Verlag Chemie G.m.b.H. Berlin. Price, R.M. 41.

The wide circle of friends of this classical "Handbuch" will appreciate the rapid appearance of the various volumes of the new edition.

The present one, dealing with the properties of strontium and its compounds, is quite up to date, the literature up to August 1931 having been covered. The subject is treated in an exhaustive way, at least the reviewer was unable to note any omission of facts described in the literature. Even the preparation and spectrographic properties of compounds of more modern interest such as those of the strontium subhalides are fully described. The editor and his collaborators deserve praise for their excellent accomplishment in the publication of this most complete compilatory work on the physical and chemical properties of elements and their compounds.

I. M. KOLTHOFF
University of Minnesota

Messentlandungsstrecken (Ionenstrecken). SIEGFRIED FRANCK. Pp. 192, viii. figs. 183. Julius Springer, Berlin, 1931. Price R.M. 18.50, bound R.M. 19.50.

This book contains a summary of the best work that has been done on the quantitative relations that obtain in disruptive discharges in gases under a great variety of conditions. The author is mainly interested in those features of these discharges that make them available and convenient for measurement over certain ranges not only of the usual electrical quantities but also of such quantities as time, speed, gas pressure, etc. Little attention is paid to the theory of the discharges which are considered, and the descriptions of the experimental methods and of the apparatus used are rather brief, but references to original sources permit the reader readily to supplement what is given. Quantitative relations are presented in numerous tables and characteristic curves, and in mathematical form as well, where this has been found possible.

Especial mention should be made of the extensive set of tables at the end of the book giving the necessary spark-gap data for the calibration of high potential voltmeters or for use in the direct determination of high voltages.

JOHN ZELENY
Yale University

Vector and Tensor Analysis. A. P. WILLS. Pp. 285+xxxii, figs. 44. Prentice-Hall, Inc., New York, 1931. Price, $5.00.

This volume is an outgrowth of the author's lectures on the subject during more than twenty years. It is designed to appeal particularly to those who are interested in the study of physics. It is likely to attract a wider circle of readers, however, for there is no other single volume in English which will take one from the very beginning so far into the subject.

The analytical part of the book is preceded by an interesting historical introduction, which traces the evolution of the vector concept from its origin in the attempt to represent complex numbers to the development of the algebra and calculus of tensors in Riemannian manifolds. The review closes with a specific reference to the work of Hessenberg in the field of tensor algebra. Conformably to Hessenberg's views, a tensor may be identified with a homogeneous multilinear form in unitary base-vectors which is invariant under coordinate transformations. A homogeneous linear form is a tensor of the first rank, or vector; a homogeneous bi-linear form is a tensor of the second rank, or dyadic. This approach simplifies materially the treatment of the theory of tensors.

The treatment of vector algebra and vector calculus is roughly equivalent to that to be found in several other English texts. Unitary vectors and reciprocal unitary vectors are employed quite freely, due, in part, to the need of accustoming the reader to these before he undertakes the study of tensors. The treatment of scalar and vector fields is conventional; the fundamental equations and transformation equations are discussed adequately. A chapter on linear vector functions and dyadics follows, which includes a number of physical examples of the use of dyadics in addition to the development of the algebra.

The last third of the book is devoted to preparation for, and presentation of tensor analysis. One chapter presents the vector algebra of generalized coordinate systems, another contains theorems concerning transformation of coordinates, and in a third chapter the vector algebra of non-Euclidean manifolds is developed. In the final chapter, the tensor is defined in accord with Hessenberg's views, as outlined earlier in this review, and the algebra is developed in accord with this definition. The Riemann-Christoffel tensor, the Ricci-Einstein tensor and the Gaussian curvature of a surface are considered at the end of the chapter.

The book will be very useful to one who wishes to gain a thorough knowledge of the subjects treated by it. The earlier chapters, on vectors and dyadics, are straightforward and give all that one needs to know in order to handle vectors easily. The chapter on tensor analysis is quite difficult reading, partly, the reviewer believes, on account of the way in which algebraic and geometric ideas are developed together. It is concise, however, and perhaps not so difficult as it appears at first sight, in view of the fact that the properties of unitary and reciprocal vectors are developed early and are used all the way through the book.

H. H. MARVIN
University of Nebraska

l'Atome de Bohr. LÉON BRILLOUIN. Pp. 363. Les Presses Universitaires de France, Paris, 1931. Price, 100 francs.

This volume is also labelled the second edition of Brillouin's "Théorie des Quanta" and is the outgrowth of his lectures at Wisconsin and Paris. It is a completely different book from the first edition, and twice its size.

The analysis is throughout by means of the old quantum theory, although the modifications in the formulas demanded by the new mechanics are often cited. There will doubtless be certain readers who will spurn the volume on this account, but in our opinion such an attitude towards the old theory is a mistake when carried too far. Calculations in the new quantum mechanics are often more thoroughly understood if their parallels in the old theory are compre-

hended, and it is only human nature to like models which one can picture, even though the picture is in reality only an asymptotic one appropriate to large quantum numbers. In particular, the model employed includes the electron spin, and so is vastly superior to the usual "classical" treatments in which spin is neglected. It is especially gratifying that the book includes a simple derivation of the "Thomas factor" 2 in the relativity-spin doublets, as the Thomas-Uhlenbeck model of the hydrogen atom appears to have become a little too completely forgotten in favor of the more rigorous and elegant but less easily visualized Dirac "quantum theory of the electron".

The first half of the volume is on the dynamical technique of the old quantum theory and includes such subjects as Larmor's theorem, action variables, adiabatic invariance, etc. Chap. VIII is welcome as an elementary presentation of the relativistic modifications of the standard theorems of analytical mechanics.

The second half is on the theory of spectral lines, and includes such subjects as multiplet structures, the Zeeman effect, etc., somewhat along the lines of Pauling and Goudsmit's book, but with less emphasis on detail in non-hydrogenic spectra. In particular very little is said about the normal terms, etc., characteristic of the various groups of the periodic table, as embodied in the well-known theory of Hund. All told, however, the book gives a very readable introductory account of the basic features of the "vector model," and is, of course, written in Professor Brillouin's characteristic, lucid style.

J. H. VAN VLECK
University of Wisconsin

Die Quantenstatistik und Ihre Anwendung auf de Elektronentheorie der Metalle LÉON BRILLOUIN. Pp. 530, figs. 57. Verlag Julius Springer, Berlin, 1931. Price, RM 42, bound RM 43.80.

The original French edition of this valuable book has already been reviewed by Professor Houston in this journal (vol. 36, p. 1674), so that it will suffice for us to comment on the new features of the subsequent German one. Some new material has been inserted on the Hall and other magnetic effects and on Dirac's method of the variation of constants, but by far the greatest alteration is the addition of about one hundred pages in Chap. VIII, called "evaluation of the mean free paths of electrons". This addition will be particularly welcomed by those who have attempted to digest the rather difficult but important papers of Bloch, Peierls, and Nordheim on the interaction between electrons and the solid's elastic vibrations. An understanding of this interaction is necessary in order to interpret theoretically the temperature variation of thermal and electrical conductivity. The new pages involve a critique of these papers and also introduce some original work which Professor Brillouin has apparently not published elsewhere. In particular he shows that the anomalous collisions postulated by Peierls lead to a T^{-2} (instead of a T^{-4} or T^{-5}) law for the electrical conductivity at low temperatures, in contradiction to experiment. Consequently Brillouin cites certain reasons why the anomalous collisions may not be as important as supposed by Peierls, thus restoring the original Bloch T^{-5} law. In the new appendix III Nordheim's method of free path analysis is compared with Brillouin's own method, which was obtained independently and is somewhat analogous. Appendix III also contains still further discussion of Peierls' assumptions.

J. H. VAN VLECK
University of Wisconsin

The Practice of Spectrum Analysis with Hilger Instruments. Pp. 62, figs. 6. Fifth edition. Adam Hilger, London 1931. Price 3s 6d.

This booklet is written for the assistance of the laboratory worker as well as for the information of those concerned with chemical analysis regarding the aid which they might obtain by the use of spectroscopic equipment. The types of problems to which spectroscopic methods are applicable are discussed in the first chapter. Following this, the equipment and experimental technique are treated briefly. Finally, methods of qualitative and quantitative analysis are outlined. The principal additions appearing in this new fifth edition are discussions of specific problems as practical illustrations of the text material, and a bibliography.

JOSEPH VALASEK
University of Minnesota

Foundations and Methods of Chemical Analysis by the Emission Spectrum. WALTER GERLACH AND EUGEN SCHWEITZER. Pp. 123, figs. 53. Adam Hilger, London 1931. Price 12s 6d.

This book, which is a translation from the German, is a critical survey of the field of chemical analysis by the emission spectrum. The many difficulties and pit-falls are carefully treated, quite in contrast with the usually optimistic treatment of the subject by those who have spectrographs to sell. The authors have made numerous analyses of various kinds to test their ideas. This work shows that a technique of spectrographic analysis may be devised which will give very accurate quantitative results without excessive difficulty. The authors particularly favor the method of "homologous lines" which they have developed. This method seems to be very good and it is discussed at considerable length with many examples. A number of useful tables are given. This is an outstanding contribution to the subject of chemical spectrum analysis.

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PROCEEDINGS OF THE AMERICAN PHYSICAL SOCIETY

MINUTES OF THE NEW ORLEANS MEETING, DECEMBER 29–30, 1931

The 33rd Annual Meeting (the 175th regular meeting) of the American Physical Society was held in New Orleans at Tulane University on Tuesday and Wednesday, December 29–30, 1931, in affiliation with Section B-Physics-of the A. A. A. S. The presiding officers were Dr. W. F. G. Swann, President of the Society, Professor H. A. Erikson, Dr. K. K. Darrow and Dr. E. A. Eckhardt. There were about 200 physicists in attendance at the meetings.

The annual joint session with Section B and the American Meteorological Society was held on Wednesday morning. The presiding officer was Professor Bergen Davis, Vice-president of Section B. The Retiring Vice-president, Professor F. K. Richtmyer, delivered an address on "The Romance of the Next Decimal Place" and he was followed by Dr. H. H. Kimball of the U. S. Weather Bureau, who spoke on "Solar Radiation as a Meteorological Factor". The attendance at this session was about 150.

On Tuesday morning and afternoon there were Mathematical Symposia held as joint sessions of the American Physical Society with the American Mathematical Society and Section A of the A. A. A. S. In the morning there were two invited papers, (1) "Stability and Instability of Physical Systems" by G. D. Birkhoff of Harvard University; (2) "The Significance of the Fundamental Concepts of Modern Atomic Theories" by W. F. G. Swann, of the Bartol Research Foundation. In the afternoon the papers were (1) "The Calculus of Variation of the Quantum Theory" by G. A. Bliss of the University of Chicago, and (2) the annual Josiah Willard Gibbs Lecture on "Statistical Mechanics and the Second Law of Thermodynamics" by P. W. Bridgman of Harvard University. These sessions were held in Dixon Hall on the Newcomb Campus and the attendance at the morning session was about 250 and in the afternoon about 275.

On Wednesday afternoon there was a joint session of the American Physical Society with Section E of the A.A.A.S. and the American Society of Petroleum Geophysicists. This was a Geophysics Program arranged and presided over by E. A. Eckhardt of the Gulf Research Laboratory. About 60 were in attendance.

The annual dinner of the Society was held on Wednesday evening at 6:30 o'clock as a joint dinner with the Geophysicists, the Meteorologists, and the American Association of Physics Teachers. There were 100 present and W. F. G. Swann presided. The guests left the dining room at the Roosevelt Hotel and went to the Municipal Auditorium to attend the meeting held in honor of the late Thomas A. Edison. President Swann presided at this meeting and the

speakers were Frank B. Jewett, Charles Edgar of the Boston Edison Electric Illuminating Company, R. A. Millikan and K. T. Compton.

Annual Business Meeting. The regular annual business meeting of the American Physical Society was held on Wednesday morning, December 30, 1931 at 9:30 o'clock in the Chemistry Building at Tulane University. The meeting was presided over by W. F. G. Swann who delivered the Presidential Address on "Reality in Physics". The President had appointed Professors Anthony Zeleny and C. W. Chamberlain to canvass the annual ballots. They reported the following electons for the year 1932:

President—W. F. G. Swann
Vice-president—Paul D. Foote
Secretary—W. L. Severinghaus
Treasurer—George B. Pegram
Managing Editor—John T. Tate
Members of the Council four year term—F. L. Mohler
Members of the Council four year term—J. H. Van Vleck
Members of the Board of the Physical Review three year term—R. C. Gibbs
Members of the Board of the Physical Review three year term—E. O. Lawrence
Members of the Board of the Physical Review three year term—J. H. Van Vleck

The ballots also showed an almost unanimous approval of the following Modifications of the Constitution which had been recommended by the Council:

A. Change Article VI, paragraph 2 to read as follows: "The Managing Editor and such other elected and appointed members as the Council may from time to time designate shall constitute the Board of Editors, and shall have charge, as designated by the Council, of the several publications of the Society. Not fewer than ten members of the Board of Editors, including the Managing Editor, shall be elected in the manner specified in Article VII."

B. Insert after Article VII two new Articles as follows: "Article VIII—Sections
   1. Members and fellows residing in any locality may, with the approval of the Council, organize a local Section for the more active furtherance of the object of the Society as stated in Article II.
   2. Any Local Section of the Society may be dissolved at the discretion of the Council."

C. Article IX—Divisions
   1. "The Council may, upon petition by members of the Society, form a Division within the Society charged with the advancement and diffusion of the knowledge of a specified subject or subjects in physics.
   2. Each Division shall elect an Executive Committee, the Chairman of which shall report its activities and needs to the Council.
   3. Any Division may be dissolved at the discretion of the Council."

The insertion of Articles VIII and IX will automatically change the number of the Article on Amendments from VIII to X.

The Secretary reviewed the four important resolutions passed at the last Annual Meeting (Proceedings, Physical Review, **37**, 454, (1931)) and reported that during the year they had all been carried out. The Secretary further reported that during the year there had been 168 elections to membership, deaths of 11 members, 26 resignations and 31 who had been dropped. The membership of the Society as of December 29, 1931, is as follows: Members: 1882; Fellows: 679; Honorary Members: 6; Total Membership; 2567.

The Treasurer presented a summary of the financial condition of the treasury of the Society. The complete audited report has been printed and distributed to all members.

The Managing Editor presented a statement of the condition of the Physical Review and the Reviews of Modern Physics and the new journal, Physics, established within the year. The journals are all being well received with a very considerable increase in the amount of material published. The complete audited statement which has been printed and distributed to all members shows that the three journals, as a combined venture, present a deficit for the year of more than $6000. This deficit is being covered very largely through the generosity of the Chemical Foundation.

Meeting of the Council. At the meeting of the Council held on Monday, December 28, 1931, twenty-four persons were elected to membership. *Elected to Membership:* Robert I. Allen, Luang Brata, Fukita Buntaro, Elizabeth Cohen, H. Richard Crane, John M. Davies, John H. Dodge, Jr., Willis Fleisher, Jr., Frederic E. Fuller, John A. Gillin, Monica Healea, Herrick L. Johnston, Norris Johnston, Frank E. Knowles, David B. Langmuir, O. C. Lester, Jr., Paul E. Lloyd, C. R. Moe, William R. Perret, Rudolph E. Peterson, Robert D. Richtmyer, Philip Rudnick, George B. Sabine and John H. Williams.

The regular scientific program of the Society consisted of 64 papers. Numbers 1, 10, 13, 17, 31, 32, 36, 43, 58, 59, 60, 61, 63, and 64 were read by title. The abstracts of these papers are given in the following pages. An **Author Index** will be found at the end.

W. L. SEVERINGHAUS, *Secretary*

ABSTRACTS

1. Thermal expansion of heat-resisting alloys. PETER HIDNERT, *Bureau of Standards, Washington, D. C.*—A comprehensive investigation on the linear thermal expansion of various heat-resisting alloys (nickel-chromium, iron-chromium and nickel-chromium-iron alloys) has recently been completed. These alloys contain 0 to 77 percent nickel, 5 to 27 percent chromium, and 0 to 82 percent iron. The coefficients of expansion of the alloys were determined for various temperature ranges between 20 and 1000°C, and the effects due to temperature, chemical composition, heat treatment, etc., were determined. Some of the expansion curves show critical regions. The data are useful in several ways. It is possible to select heat-resisting alloys which have the same coefficients of expansion for a given temperature range as other materials, for example, brass, copper, porcelain, steel, etc. It is possible to predict the coefficients of expansion of similar new alloys. It is also possible to determine the heat treatment suitable for each type of alloy for a specific purpose as governed by the desired structure. The data (including names and chemical compositions of the alloys) will be published soon in Research Paper of the Bureau of Standards No. 388. This publication will be available through the U. S. Government Printing Office, Washington, D. C., or at Government depository libraries in many cities.

2. Heat treatment of fine metallic suspensions. N. N. ZIRBEL AND A. B. BRYAN, *The Rice Institute.*—When a suspended system is supported by a fine wire the equilibrium position usually changes slowly for a long time after the load is applied. The equilibrium position also changes with temperature. It is found that both of these disturbing factors can be eliminated by a suitable heat treatment of the wire. Observations have been made on tungsten and platinum-iridium wires of sizes suitable for use in the Eotvos torsion balance.

3. The effect of Brownian motion on the useful sensitivity of the resonance radiometer. G. A. VAN LEAR, JR., *University of Oklahoma and* J. D. HARDY, *National Research Fellow, University of Michigan.*—A general treatment of the effect of Brownian motion on the useful sensitivity of the resonance radiometer is given which takes into account the effect of electromagnetic damping. The treatment follows the lines of that given by Hardy in his first paper on the instrument, but is carried through in general terms (the assumption of constants for a specific instrument is not necessary, as heretofore), and leads to a result which depends upon, aside from the temperature, only the resistance of the instrument and the time required to take an observation. When expressed in these terms, the limitation is practically identical with that for the critically-damped galvanometer. Results are also given for certain variations of the instrument as originally described, the limitation found being virtually the same in all cases. However, the advantages remaining to the resonance radiometer for high sensitivity work are pointed out.

4. A kinetic theory of the elasticity of highly elastic gels. E. KARRER, *Medical School, Western Reserve University.*—Studies of several physical properties of colloid systems point to general theory to account for the great elasticity of rubbery gels. Fluidity, $\phi = A - q/T$. T is temperature; q, energy factor; A, number of moving elements, etc. Changes of constants, A and q with concentration and mastication suggest long filamentous molecules of rubber hydrocarbon, that may entrain much solvent. To account for change of viscosity with mechanical agitation (thixotropy) interplay between chaotic forces of thermal agitation, and of local asymmetrical orientating forces of attraction of molecules or particles is envisaged. Orientating forces are adsorptive, but may be those of primary valence, as in litharge-glycerine, electric charges; or may be mechanical, as in stretching and flowing of rubber, or magnetic. Rubber and muscle contain long thin molecules, which in thermal equilibrium are anything but straight. (This may be called a principle of maximum mechanical or geometrical chaos.) Stretching forces produce straightness and tautness. Lateral cohesive forces must be less than end-on forces. Stiffness and rididity depend also on shape of molecules. Side chains and polar groups affect this markedly, as evidenced by studies of nature and measurement of frictional forces. Stretching eliminates longitudinal degrees of thermal freedom, therefore, heating.

5. An extension of the application and interpretation of the Faraday fluxes. ANTHONY ZELENY, *University of Minnesota.*—The elemental electric fields about electrons and protons are treated as physical entities and inseparable parts of the individual charges. These elemental fields extend indefinitely, interpenetrate freely, and possess inertia and power to transmit energy. An observed electric field is the resultant of such superposed elemental fields which retain their individual identities. A magnetic field is a property of a moving electric field which it possesses by virtue of motion. The term magnetic flux applies to this property and not to an independent physical entity. The magnetic field about a conductor exists without an apparent electric field because the resultants of the two kinds of elemental fields neutralize each other's action on electric charges at rest. Accelerating electrons in a conductor produce a distortion in their resultant negative field. This distortion has an electric component whose action on charges is not neutralized by the opposing positive field. It carries energy outward which it continues to transmit to the as yet stationary part of the field giving it velocity and thereby the property of a magnetic field. The observed intensities of the magnetic fields about loops and charged rotating spheres show that the elemental fields move with their lines of force always parallel to themselves. These facts and points of view enable the well established facts of electricity and magnetism to be clearly explained in terms of definite physical concepts.

6. On the origin of the solar system. Ross Gunn, *Naval Research Laboratory.*—A new account of the formation of the solar system, based on the rotational evolution of a single star, is given which describes the system in some detail and avoids the major difficulties encountered by earlier investigators. Electromagnetic effects have been shown by the author to permit the angular velocity of a star to increase until the star breaks into two components of comparable mass. The component stars are thermally asymmetrical and momentum is radiated more rapidly from the hot face than from the cool. This important new effect, which is quantitatively satisfactory, adds kinetic energy and angular momentum to the companion stars (in a manner analogous to the mechanism of a skyrocket) and may operate to separate the stars to infinity. Applying this to the solar system, the parent semiliquid sun is supposed to have divided and lost its companion. While each companion was inside the Roche limit of the other centrifugal and tidal forces broke off the planets. These in turn immediately broke up and formed the planetary satellites. Tides and tidal couples transferred the momentum of axial spin of the two component stars to that of orbital momentum, while the planets because of their small size largely escaped the effects of this process. Planetary rotations play an important role in the theory. The account replaces the earlier improbable and "accidental" theory by a systematic evolutionary process which is probably quite common in the Universe.

7. Resistance bridge thermometer. Loraine Decherd and Arnold Romberg, *University of Texas.*—A resistance thermometer intended as a secondary standard is described, in which all four branches of the bridge, two of copper and two of manganin, are at the temperature of the bath. All resistances are permanently joined by hard solder or welds, with multiple leads, and mounted on a rigid support. Moving contacts and flexible resistances are absent. The thermometer is simpler to use than other resistance thermometers, and requires no auxiliary apparatus other than battery and galvanometer. The last two figures of a temperature are read by deflection. Simplicity of calibration is secured by equality, at all temperatures, of the two parallel branches of the bridge between galvanometer terminals.

8. Production and recording of continuous seismic waves in the ground. W. R. Ransone, *University of Texas.* (*Introduced by Arnold Romberg.*)—The first recorded data on the transmission of continuous seismic waves of variable frequency are presented. A discussion of the apparatus used and method of setting up the waves in the ground and recording them is given. The records indicate that the velocities of the continuous waves are not the same as that of the first impulses from impact (dynamite) excitation; that interference patterns exist, and that the ground may be resonant to some frequencies. Feasibility of using the method of continuous waves in geophysical exploration is suggested.

9. A simple ultracentrifuge. J. W. Beams, *University of Virginia.*—The method of rotating the centrifuge is a modification of that used by Henriot and Huguenard, (C.R. **180,** 1389 (1925) and J. de Phys. et Rad. **8,** 443 (1927)), and similar to one previously described for obtaining high rotational speeds, (Rev. Sci. Inst. **1,** 667 (1930) and Science **74,** 44 (1931)). A simple arrangement has been devised by which the light absorption and approximate index of refraction of the materials being centrifuged can be measured as a function of the distance from the axis of rotation of the rotor at full speed. Mounted in a channel cut along a diameter of the top of the rotor is a Pyrex or quartz rod polished flat on its ends. The rod is ground along a narrow strip parallel to its axis which appears illuminated when light enters from either end. Above and next to this strip is mounted a Pyrex tube containing the substances under investigation, through which the strip is observed. With this arrangement centrifugal forces of the order of $10^5 \times$gravity have been obtained. However, this should not be the upper limit for with small all-metal rotors forces of the order of a million gravity have been obtained under favorable conditions. Simple methods of measuring the approximate temperature and rotational speed are discussed.

10. A laboratory apparatus for the determination of the acceleration of a freely falling body. P. H. Carr and R. M. Bowie, *Iowa State College, Ames, Iowa.*—There has been a need for an inexpensive, laboratory method for determining the acceleration of a freely falling body. Such a device has been developed for use in our elementary course. This apparatus is composed of only

such things as Ford coils, electric lamps and potassium iodide soaked paper and operates on 110 v, 60 cycle, alternating current. A ball, suspended from an electromagnet, is released by a key. During the time of fall, spots are made at the rate of 120 per second on the potassium iodide paper. At the end of the fall the ball opens a switch, thus concluding the record. In the hands of elementary students results obtained by this method agree with the accepted value to within two percent.

11. Spatial energy decay due to absorbing boundaries. H. H. GERMOND, *University of Florida.*—A fundamental error in Franklin's derivation of the spatial energy decay due to absorbing boundaries is demonstrated and corrected. The average energy density over the surface is derived in terms of the average throughout the space.

12. Note on the transmission and reflection of wave packets by potential barriers. L. A. MACCOLL, *Bell Telephone Laboratories.*—In previous studies, by the methods of wave mechanics, of one dimensional motion of particles in cases in which there are intervals in which the value of the potential energy function $V(x)$ exceeds the value of the total energy E, attention has been confined to wave functions of the form $f(x, E) \exp(-2\pi iEt/h)$. In the present note wave packets are considered, instead of these trains of waves. The function $V(x)$ is taken as follows: $V(x)=0$ for $x<0$ and for $x>a$, and $V(x)=V_0>0$ for $0<x<a$. A wave function is set up which initially represents a wave packet moving toward the point $x=0$ from the left. The separation of the incident packet into a reflected packet and a transmitted packet is studied. It is found that the transmitted packet appears at the point $x=a$ at about the time at which the incident packet reaches the point $x=0$, so that there is no appreciable delay in the transmission of the packet through the barrier.

13. Quantum mechanics of lithium hydride. MORRIS MUSKAT, *Gulf Research Laboratory,* AND ELMER HUTCHISSON, *University of Pittsburgh.*—Quantum mechanical calculations have been carried through for the normal state of the lithium hydride molecule. Two cases were considered. First, the radial eigenfunction of the valence electron of lithium was taken as nodeless as given by Slater. Second, the function derived by Guillemin and Zener with a node at $0.18a_0$ was used. In both cases the K electrons of lithium were neglected. The results are as follows:

Type of eigenfunction	Equilibrium distance in Angstroms	Heat of dissociation electron volts/molecule	Fundamental frequency in cm^{-1}
Slater	1.427	2.30	1.4×10^3
Guillemin and Zener	1.454	2.21	1.4×10^3
Experimental values	1.6	2.56	1.380×10^3

These results are seen to be in reasonable agreement considering the approximations made, and justify at the same time the use of the simpler and nodeless Slater functions in other calculations.

14. The absorption and emission of sodium light by sodium flames. T. W. BONNER, *The Rice Institute. (Introduced by H. A. Wilson.)*—The variation of the luminosity of a sodium flame with the concentration of the sodium and the thicknes of the flame has been measured with a spectrophotometer. The flame more than filled the angular aperture of the photometer so that the distance of the flame or parts of it made no difference. In agreement with previous work by Gouy, H. A. Wilson and G. L. Locher it was found that the luminosity is a function of the product of the concentration and the thickness or of the mass (M) of sodium per cm^2. This function is proportional to M when M is very small but increases less rapidly than M when M is large. It is only very roughly proportional to $M^{1/2}$. These results do not agree with the recent ones of C. D. Child, (Phys. Rev. **38,** 670 (1931)). Reasons for this discrepancy are suggested.

15. Excitation of atomic mercury by electron impact. W. G. PENNEY, *University of Wisconsin. (Introduced by J. H. Van Vleck.)*—The probability of excitation by electron impact of the four P levels (2^1P_1, 2^3P_2, 2^3P_1, 2^3P_0) of Hg has been calculated. It is found that, although

with increasing velocities the excitation of two of the triplet levels vanishes compared with that of the singlet, that of the middle triplet level approaches a small constant value, which can be computed from the singlet-triplet separation. An estimate is made of the relative excitation of all four P levels for fairly slow electrons, and these are all of the same order of magnitude. A brief comparison with experiment is given.

16. The Zeeman effect of the K II spectrum. ALBERT E. WHITFORD, *University of Wisconsin.*—The Zeeman effect of the $p^5 \cdot 4p \rightarrow p^5 \cdot 4s$ transitions of K II has been studied in an effort to throw light on the failure of the $p^5 \cdot 4s$ configuration to obey Houston's multiplet relations and of the $^3P_2 - {}^3P_0$ interval to follow the regular doublet law. The magnetically resolved lines from a Back vacuum arc were photographed in the 3rd order of a 21 ft. 15,000 line concave grating in a Rowland mounting. Not all of the Zeeman patterns were completely resolved, but g values were obtained from triplet and quartet blends by the method of Shenstone and Blair. Analysis of the results showed that the classification of deBruin and Bowen is correct. The g values of the p terms follow closely those found by Back for Ne I and obey the g sum rule within the limits of experimental error. The g sums for the s terms based on completely resolved patterns are definitely greater than those predicted by the sum rule. The g sum rule would not be expected to hold if the anomalous intervals among the terms labeled $p^5 \cdot 4s$ are caused by interaction between the configurations $p^5 \cdot 4s$ and $p^5 \cdot 3d$. The levels of these configurations overlap in K II and also in Rb II, where a similar anomaly has been noted.

17. Pressure shift of spectral lines. HENRY MARGENAU, *Yale University.*—The pressure shift of spectral lines, unexplained by the usual theories of pressure broadening, together with other interesting effects of pressure upon the appearance of absorption lines, can be adequately treated on the basis of the following theory, the details of which are worked out for the absorption of λ2537(Hg) in foreign gases. (Experiments by Füchtbauer, Joos, and Dinckelacker, Ann. d. Physik **71**, 204(1923).) The wave mechanical interaction energy between an Hg atom and an unexcited foreign atom is computed as a function of the distance of separation (1) for the case in which the Hg atom is unexcited, (2) when the Hg atom is in the $2p_2$ level. The perturbation energy is in both cases proportional to $1/R^6$, but the coefficient in case (2) is larger. This implies that, on the average, the energy difference between the two states of the Hg atom is slightly smaller than that corresponding to λ2537A (red shift). Statistical considerations permit an estimate of the shift and broadening, the results being in satisfactory agreement with experiment. The shift is proportional to the density of the perturbing gas. The theory allows blue shifts in cases which, apparently, have not been tried experimentally.

18. Active nitrogen. JOSEPH KAPLAN, *University of California at Los Angeles.*—Striking similarities are pointed out between two independent experiments on active nitrogen. The first experiment is the production of metastable nitrogen molecules in nitrogen-mercury mixtures, by the quenching of the second positive bands of nitrogen by mercury atoms (Phys. Rev. **37**, 226, (1931)), and the second one is the production of the nitrogen afterglow in uncondensed discharges (Phys. Rev. **37**, 1004, 1931). Although no visible glow was observed in the Hg-N_2 experiments, the presence of active nitrogen was shown by the excitation of the violet cyanogen bands, the cyanogen having been produced in the discharge-tube reaction $CO + N(^2D) = CN + O$. The strong second-positive bands of N_2, which are always very intense in the usual active-nitrogen producing discharges, were nearly completely missing in these experiments. There was a strong enhancement of certain band heads of the first-positive group of N_2, which has been correlated with predissociation. The appearance of the afterglow in the uncondensed discharge is probably due to the change in surface brought about by constant running of the tube. The main significance of these experiments lies in the fact that the afterglow has been produced under conditions which disagree violently with the ones usually necessary for the production of active nitrogen.

19. The wave-length of the molybdenum and copper K series. J. A. BEARDEN, *Johns Hopkins University.*—The quantum theory of dispersion as developed by Kronig, Kramers, Kallman and Mark may be written for incident frequencies ν greater than the natural frequencies ν_s of the refracting electrons in the form

$$\lambda = \delta^{1/2}\left[\frac{\rho}{w}\cdot\frac{e}{m}\cdot\frac{F}{2\pi}\sum_{1}^{s} N_s\left\{1+\frac{\log(x^2-1)}{x^2}-\frac{2\pi q}{x^3}\right\}\right]^{-1/2}$$

where $\delta = 1-\mu$, ρ the density, w the molecular weight, e/m the ratio of charge to mass of the electron, F the Faraday constant, N_s the number of electrons per molecule of natural frequency ν_s, $x = \nu/\nu_s$, $q = k/\nu_s$ where k is the damping factor which can be obtained from the atomic absorption coefficient. The value of the bracket term is independent of small changes in ν and ν_s. Since the x-ray wave-lengths, as determined by crystals and ruled gratings, differ by 0.25 percent, we may use this relation to indicate which is correct. The writer has recently made some precise measurements of the refraction of the molybdenum and copper K series in a prism of quartz. The results are given in the following table.

Method	$\delta\times10^6$	λ(Dispersion)	λ(Crystal)	λ(Grating)
1	8.553	1.536A	1.538A	1.542A
1	6.971	1.388	1.389	1.392
2	8.560	1.537	1.538	1.542
2	6.976	1.388	1.389	1.392
1 & 2	1.805	0.7089	0.7093	0.7109
1 & 2	1.432	0.6315	0.6314	0.6328

It is difficult to believe that such an agreement between the wave-lengths as determined by dispersion and by crystals is entirely fortuitous. Thus it appears that the optical diffraction theory is not valid when applied to x-ray wave-lengths.

20. A ruler and chart method of interpreting x-ray oscillation photographs and an application to cerussite. LUCIEN LACOSTE, *University of Texas. (Introduced by M. Y. Colby.)*—A ruler and chart method of obtaining the reciprocal lattice projections of planes appearing on an oscillation photograph has been devised. The method is similar to Gruner's (Amer. Min. **13,** 123, (1928)) except that it eliminates all calculations and reduces the probability of working errors without any loss of accuracy. Planes whose indices are uncertain are identified, by determining the Bragg angle. This is done by taking oscillation photographs by a method in which the photographic plate is oscillated in synchronism with the crystal about an axis prependicular to the photographic plate. A comparison of this type of photograph with the usual type gives the Bragg angle. This method of identifying planes of uncertain indices can also be used in conjunction with Bernal nets (Proc. Roy. Soc. L. **113A,** 116). The ruler and chart provide a simple means of making these nets. The ruler and chart method has been used in a study of cerrussite, with the following results:

$$a = 5.17\text{A},\ b = 8.47\text{A},\ c = 6.13\text{A}.$$

The unit cell contains four molecules. The space group is $2\text{Di}-16$.

21. X-ray diffraction patterns of mixtures. M. Y. COLBY, *University of Texas.*—Experiments have been carried out to duplicate those of Roy W. Drier (Phys. Rev. **37,** 712, 1931), in which powder photographs of mixtures of Zn and Cu at room temperature invariably exhibited eight lines that did not appear on the composite diffraction pattern of the components. These extra lines were attributed to α-brass. By using freshly prepared zinc and copper filings (200 mesh) sealed in Pyrex capillary tubes, powder photographs have been obtained with the General Electric x-ray diffraction apparatus. They show no extra lines. In agreement with Kenney and Aughey, (Phy. Rev. **38,** 1388, (1931)) the photographs of the mixture are identical with the composite photographs of the components in every case. Using a mixture of freshly prepared copper dust and old zinc dust, eight lines appear, belonging to neither Cu nor Zn. These "extra" lines, however, correspond exactly to the eight strong lines or zinc oxide.

22. Crystal structure of ammonium bicarbonate. R. C. L. MOONEY, *University of Chicago.*—X-ray data obtained from laboratory-grown crystals, of NH_4HCO_3 show that the symmetry is orthorhombic, the unit cell dimensions are $a = 7.29$ A.U, $b = 10.79$ A.U, $c = 8.76$ A.U; there are eight molecules in the unit cell, and the space group is Pccn (V_h^{10}). Groth gives the axial ratios as 0.6726:1:0.3998. Those obtained experimentally are 0.676:1:2 (0.406). Relative intensity considerations indicate that the CO_3 groups in the structure lie approximately in planes parallel

to the *a*-face, in agreement with reported optical properties. (Birefringence and orientation of optical axes.) The hydrogen atoms cannot be fixed by means of intensity data, but there is strong evidence that those not belonging to the NH_4 groups lie between oxygens of different CO_3 groups. The dimensions of the CO_3 groups are, within the limit of the observations, essentially the same as in the normal carbonates.

23. The change in thermal e.m.f. produced by a magnetic field. H. E. Banta, *Rice Institute.* (*Introduced by C. W. Heaps.*)—The change ΔE, due to a magnetic field H, of E the *e.m.f.* of a thermocouple is measured in these experiments. A commutator rotating at constant speed allows a current to flow through the couple, thus producing a temperature gradient between the junctions by the Peltier effect. This exciting current is then cut off by the commutator, and the couple connected to a very sensitive potentiometer for a short time. This process is automatically repeated every 2.5 seconds. The potentiometer is adjusted so that when the couple is connected to it the galvanometer does not jump. The two junctions are copper on a metallic crystal. The quantity $\Delta E/E$ is determined as a function of magnetic field, of temperature, of direction of field, direction of crystal axis, and of direction of heat flow. The present experiments are on a pure bismuth crystal; it is proposed to extend the investigation to other crystalline metals.

24. Low frequency vibrations in Rochelle salt and quartz plates. W. G. Cady, *Wesleyan University.*—In continuation of previous work (Phys. Rev. **33,** 278 (1929)) observations of frequency have been made on Rochelle salt resonators with flexural vibrations in planes perpendicular to all three axes and with torsional vibrations about the X axis. Best values to date for Young's modulus parallel to the X, Y and Z axes are 1.99 ± 0.06, 2.88 ± 0.06, and 2.91 ± 0.01, respectively, all multiplied by 10^{11} dynes/cm^2. For bars at 45 degrees to the YZ, ZX and XY, axes, the values are 3.02, 0.98 and 2.52×10^{11}. The observed rigidity appears to be only $0.49 + 10^{11}$. The temperature coefficient of frequency is very large, from 400 to 1400 parts in a million per degree C. However, for bars at 45 degrees to the Y and Z axes, the frequency-temperature curve has an inflection between 21 and 23 degrees C, so that for a narrow range of temperature the coefficient is practically zero. Similar frequency tests have been made with quartz resonators, using flexural vibrations in planes perpendicular to all three axes, also torsional vibrations about the Y and Z axes. A quartz flexural vibrator 9.3 cm long has been made to serve as a master oscillator at only 3000 cycles/sec.

25. Further study of effects of intense audio-frequency sound. Newton Gaines and Leslie A. Chambers, *Texas Christian University.*—The magnetostrictive nickel tube vibrator mentioned in Abstract 42 (Phys. Rev. **37,** 109 (1931)) has been improved. Explosive rupture of water fleas due to one second's exposure to the sound has been observed. The bactericidal effect has been extended to organisms present in raw milk, and there has been developed a device for the continuous sterilization of milk by sound.

26. The production of high speed protons without the use of high voltages. Ernest O. Lawrence and M. Stanley Livingston, *University of California.*—A method for the multiple acceleration of charged particles to high velocities described recently before this society (E. O. Lawrence and M. S. Livingston, Phys. Rev. **38,** 834 (1931)) has now been brought to a stage of development where it can serve in experimental studies of atomic nuclei. The present experimental arrangement automatically focusses the beam of ions all along their spiral paths as they are successively accelerated; practically no ions are lost in the course of acceleration. With the present apparatus, currents of about 10^{-9} amp. of 1,100,000 volt protons have been generated. A larger apparatus is under construction for the production of protons having greater kinetic energies.

27. Current-voltage and thermal characteristics of the copper oxide rectifier. W. B. Pietenpol and G. W. Presnell, *University of Colorado.*—It has been suggested (Gentry, Science, Sept. 23 (1927)) that the relation between current and voltage for the copper oxide rectifier may be represented by the space charge equation, $I = kV^{3/2}$. Measurements have been

made over a wide range of voltages and the slope of the logarithmic curve indicates that the space charge equation applies to a reasonable degree of accuracy for high voltages. At very low voltages Ohm's Law is obeyed while at intermediate voltages, slopes of 0.8 and 4, in the high and low resistance directions respectively, indicate the influence of an additional factor. The application of a temperature gradient to the copper, copper-oxide surface produces a current in the direction of heat flow. The temperature gradient resulting from the passage of a current therefore tends to aid the rectification, and this factor is suggested as an explanation for the variation in the slopes of the curves at intermediate voltages. A careful determination of the variation in resistance with temperature at extremely low voltages has been made. The results obtained by previous experimenters have been verified for ordinary voltages.

28. Generation of combination and harmonic frequencies by linear and non-linear vacuum tube circuits. C. P. Boner and Marian O. Boner, *University of Texas.*—An audible beat method is used to measure amplitudes of the components of alternating current in a triode when the grid circuit contains electromotive forces at two frequencies. With resistance load in the plate circuit, current at the summation and difference frequencies are equal in amplitude, regardless of the equation of the characteristic. By using a parabolic section of the characteristic, measured amplitudes of these combination currents check theoretical values. As the dynamic characteristic is straightened by addition of impedance in the plate circuit both combination currents disappear, and no tone at a "beat frequency" remains. Results indicate that there is no "beat tone" generated in a receiving system, linear or non-linear. Further, the output of a vacuum tube amplifier stage contains a far smaller percent of harmonic and combination frequencies when high quality transformer coupling is used than when resistance coupling is used, provided transformer secondaries carry no load.

29. Harmonic analysis of the plate current in a vacuum tube circuit. S. Leroy Brown, *University of Texas.*—The harmonic components of the plate current which flows when the control or grid-voltage is varied sinusoidally may be determined from the operating characteristic of the tube. The operating characteristic is analyzed as a cathode ray oscillogram with the aid of the Wiebusch Analyzer (J.O.S. and R.S.I. **15,** 355 (1927)). The analysis of a section of the static characteristic gives the amplitudes and phase relations of the harmonic components in the plate current that are produced by a sinusoidal grid voltage, the amplitude of the alternating grid voltage and the grid bias being determined by the section of the characteristic curve that is selected. When there is a load in the plate circuit, the operating characteristic may be obtained with a cathode ray oscillograph and the analysis of the oscillogram gives the harmonic components of the plate current for the particular operating conditions and load impedance.

30. The calculation of detection performance in a vacuum tube circuit for large signals. J. P. Woods, *University of Texas.* (*Introduced by S. Leroy Brown.*)—It is mathematically proven that a detector tube which has a broken straight line for its plate-current, grid-voltage static characteristic will detect the standard radio signal without distortion, regardless of signal strength. The plate detection performance of a tube having a given curve for its static characteristic can be calculated from the extended power series which represents the characteristic. The power series analysis of the curve is obtained from a Fourier series analysis by a method which saves labor and is more accurate than the method of simultaneous equations. Thus, by using twelve or fifteen terms of the power series instead of only the first two or three, and by setting up special formulae, detection performance can be calculated for any signal strength and any modulation. The method is applicable to the tube alone, to a circuit containing the tube and external resistances, and may be applied to any similar non-linear receiving system.

31. Methods of detecting molecular rays. J. Tykocinski-Tykociner, *University of Illinois.*—The usual methods of detecting molecular beams by the use of manometers and thermocouples is fraught with difficulties due to galvanometer drifting which is produced by radiation and spurious changes in pressure. The new methods are designated to eliminate these difficulties by periodically interrupting the molecular beam. A vibrating or rotating shutter may be used for this purpose. In its simplest form the vibrator consists of a fine steel wire inserted

perpendicularly to the direction of the beam and actuated by an a.c. electromagnet placed outside the vacuum envelope. Beside the usual types of manometric receivers, a condenser-microphone may be used, whose vibrating part consists of a wire tuned to the frequency of interruption. By known methods of amplification any degree of sensitivity in the conversion of pressure variations into a.c. can thus be obtained. Also a thermocouple or a fine wire may be directly subjected to the bombardment of such molecular rays. Periodic variations of temperature are in this case converted into a.c. These methods are especially adaptable in connection with a selector which by its action subdivides a continuous beam into sequent groups of molecules of definite velocity. No additional shutter is therefore necessary when a selector is used. Two selectors, one for a frequency of 500, the other for 8000 per sec. are being tested in connection with the above methods of detection.

32. Effect of magnetic field on reflected electron beams. E. RUPP AND L. SZILARD, *German General Electric Co.* (*Introduced by E. P. Wigner.*)—Electron beams with velocities between 70,000 and 220,000 volts were reflected from crystals of heavy metals and subsequently subjected to longitudinal and transverse magnetic fields. The direction of polarization of the beam in a longitudinal field is shown to rotate according to the Larmor precession. The effect in the transverse field is more complicated but can be fully accounted for by the theory of the spinning electron. Further experiments are in progress with special reference to relativistic effects.

33. The nuclear spin of caesium by the method of molecular beams. I. I. RABI, *Columbia University.*—A beam of caesium atoms was sent through a weak and inhomogeneous magnetic field. The deflection pattern was observed and compared with the pattern obtained from a beam of potassium atoms in the same field. To obtain sufficiently large deflections a very long path was used (36 cm). At fields where the potassium beam is strongly split the caesium shows only a broadening. It is only at much larger fields that the caesium beam is split. At the temperature used the patterns should be entirely similar. The results show the presence in caesium of a nuclear spin which can be rather easily evaluated from a knowledge of the magnetic field and its gradient.

34. An isotope of hydrogen of mass 2 and its concentration. HAROLD C. UREY, F. G. BRICKWEDDE, AND G. M. MURPHY, *Columbia University and The Bureau of Standards.*—The proton electron plot of atomic nuclei (Urey, J. Am. Chem. Soc. **53,** 2872; Johnston, ibidem, **53,** 2866) indicates that hydrogen isotopes of mass 2 and 3 may be expected to exist. The discrepancy between the atomic masses of hydrogen as determined by Aston and by chemical methods indicates that higher isotopes of hydrogen may be present (Birge and Menzel, Phys. Rev. **37,** 1669 (1931)). A calculation of the relative vapor pressures at low temperatures of the molecules H_2^1, H^1H^2, and H^1H^3 from theory shows that the heavier molecules should be rapidly concentrated in a residue from the evaporation of hydrogen near the triple point. One of us (F.G.B.) prepared such a sample. The other two authors investigated it for atomic lines of hydrogen atoms of masses 2 and 3. It is found that $H\beta$, $H\gamma$, and $H\delta$ are accompanied by weaker lines agreeing within experimental error (about 0.02 A) with the calculated positions for an isotope of mass 2. The isotope lines have about the same breadth as the main lines. These are found in ordinary hydrogen with intensity about 1/4000 of the main lines and in the residue from the evaporated hydrogen with distinctly greater intensity indicating an abundance of about 1/800. No evidence for the existence of H^3 has been found. Work on the $H\alpha$ line is in progress. Work on the further concentration and on the molecular spectrum is planned.

35. On the range of fast electrons and neutrons. J. F. CARLSON AND J. R. OPPENHEIMER, *Berkeley, California.*—We have made calculations of the ionizing power of electrons and protons with velocity very close to that of light, taking adequate account of the retardation of the forces between the particle and the electrons in the matter through which the particle is passing, and of the binding of these electrons in atoms. If M be the rest mass of the particle and ϵMc^2 its energy, then for very large ϵ, (1) the number of ions produced per centimeter path increases with $\ln \epsilon_i$, (2) the range of the particle is just one fourth of the mean distance, which, according

to the Klein-Nishina formula, a gamma ray of the same energy should travel before its first Compton scattering. We have also computed the ionizing power of the neutrons, which were suggested by Pauli as elements in the structure of the nucleus. The number of ions produced by fast neutrons is sensibly independent of the velocity, and depends only on their magnetic moment. In conjunction with the experiments of Bothe, Kolhoerster, Rossi and Mott-Smith, the results (1) and (2) show that the ionizing radiation associated with the cosmic rays cannot be either primary of secondary electrons or protons. It is suggested that if these rays are neutrons, thin cloud-chamber tracks should be found accompanying the beta-ray tracks in a beta-ray radioactive disintegration.

36. On the use of the Wilson cloud chamber for measuring the range of alpha particles from weak sources. F. N. D. KURIE, *Yale University.*—A large Wilson cloud chamber is operated by a synchronizing mechanism similar to that described by Blackett. A single lens camera is used which takes two sharp photographs of the whole volume of the chamber by mirrors which are so arranged that they are equivalent to photographs taken by two cameras at right angles, and so enable one to study tracks inclined to the plane of the chamber. The conditions to be satisfied by the camera are discussed. The photographs are examined by replacing the developed film in the camera, using this as a projection apparatus. The two images can be caught on a suitably oriented photographic plate as one image of the same size as the original track. This may be measured in a comparator. The α-particle source may be quite large and is mounted in the center of the chamber. Tests of the method have been made, by photographing glass fibers of known length and also by determining the range of polonium α-particles. It will be applied to the range of uranium α-particles. The temperature in the chamber has been carefully studied over the cycle and over long runs to ensure accuracy in reducing the ranges to standard conditions.

37. Inelastic and elastic electron scattering in argon. A. L. HUGHES AND J. H. MCMILLEN, *Washington University, St. Louis, Mo.*—The energy distributions of electrons, scattered in argon at 10°, and having lost various amounts of energy, have been measured for 50 to 200 volt primary electrons. (The energy losses included the excitation loss, 11.6 volts, the ionization loss, 15.5 volts, and still greater losses.) It was found that the greater the energy of the primary electron, the greater was the relative probability of the larger energy losses. The angular scattering curve (5° to 35°) for all the inelastic collisions is *steeper*, the *greater* the energy of the primary electron. These angular scattering curves are *steeper* the *less* the energy *lost* in the collision. Angular *elastic* scattering curves were obtained for primary electrons having energies between 50 and 550 volts and plotted against $(\sin\theta/2)/\lambda$ (where λ is the De Broglie wave-length and θ the angle of scattering). The curves for the higher velocities are practically superposable, as they should be on Mott's theory. There is satisfactory agreement between the scattering curve obtained experimentally with 550 volt electrons, and that calculated on Mott's theory. Maxima in the angular distribution curves for 50 and 100 volt electrons were found at 100° and 90° respectively.

38. Distribution of electrons ejected in ionization of argon atoms. J. H. MCMILLEN AND A. L. HUGHES. *Washington University, St. Louis, Mo.*—Theoretically the energy of impact of an electron ionizing an atom, in excess of that necessary for ionization, may be divided in any way between the faster ionizing, and the slower ejected, electrons. Energy distribution curves for the electrons ejected by 50, 100 and 200 volt primary electrons show that the smaller the energy of ejected electron the more probable is its occurrence. This is in qualitative accord with the result that the less the energy lost by the ionizing electron the more probable is this kind of collision. The total number of 3 volt ejected electrons is of the same order as the total number of ionizing electrons which have lost 3 volts more than the ionization energy. The angular scattering curves for the low velocity ejected electrons (except for a small maximum near 120°) show a tendency towards a uniform distribution in angle, in striking contrast with the concentration of the ionizing electrons in the onward direction. The position of the small maximum in the ejected electron scattering curves depends on the energy of the colliding electrons and on the energy of the ejected electrons.

39. Photoelectric emission from cadmium and mercury. DUANE ROLLER AND HUGHES ZENOR, *University of Oklahoma.*—This paper describes the photoelectric properties and the methods of preparing thin films of pure cadmium and of pure mercury deposited on oxidized iron and on glass. New experiments on the effects of contamination on the photoelectric behavior of mercury in bulk are also described.

40. The compound photoelectric action of x-rays in oxygen and argon. GORDON L. LOCHER, *The Rice Institute.*—When an atom has a K-electron ejected by x-rays, an outer electron falls into the vacant orbit, accompanied by the emission of a quantum of K-radiation characteristic of the atom. The quantum may escape (simple photoelectric action) or eject an outer electron from the same atom (compound action). In the experiment described here, the "K-fluorescence yield", that is, the ratio of the number of cases of simple-action to the total number of both kinds for K-ionized atoms, has been determined by the direct method of counting the relative numbers of single and double tracks obtained by passing a beam of 0.709 A.U. x-rays through a Wilson cloud-apparatus containing the gas under investigation. For oxygen, 900 pairs of stereo-photographs of tracks, in an atmosphere composed of hydrogen gas and water vapor, were collected and examined; of these 14.4 percent were single and 85.6 percent double. Since 85 percent of all photoelectrons should come from the K-shell, the indicated fluorescence yield is zero, which means that no fluorescent K-radiation is emitted by oxygen. By similar procedure, the fluorescence yield of argon has been determined from 500 stereo-photographs of tracks produced in an atmosphere composed of argon, hydrogen and water vapor.

41. The photoelectric and thermionic properties of palladium. W. W. ROEHR AND L. A. DUBRIDGE, *Washington University, St. Louis.*—The photoelectric threshold of a filament of pure palladium foil was studied during 1000 hours of heat treatment in the highest attainable vacuum. It shifted from an initial value of less than 2300A to a maximum value of more than 3022A and finally approached a steady value of 2486A (4.97 volts), which could not be changed by further treatment. This value is apparently characteristic of clean palladium. The thermionic work function in the final state was found to be 4.99 ± 0.04 volts, in good agreement with the photoelectric value. The coefficient A was close to the theoretical value of 60 amp./cm^{2}deg^2. The photoelectric currents excited by monochromatic light increase with temperature over the range 300° to 1070°K, the rate of increase being greater for frequencies near the threshold. The photocurrent-frequency curves taken at the higher temperatures approach the axis asymptotically. All the results are shown to be in excellent agreement with Fowler's theory, and an analysis of the data for 8 temperatures by his method yields a *true* photoelectric work function of 4.97 ± 0.01 volts, independent of temperature.

42. A further experimental test of Fowler's theory of photoelectric emission. L. A. DUBRIDGE, *Washington University, St. Louis.*—The new theory of photoelectric emission proposed by Fowler (Phys. Rev. **38,** 45, 1931) has been shown to be in excellent agreement with observations on a number of clean metals. The theory predicts that the photocurrent-frequency curves should approach the axis asymptotically, so that there is no sharply defined threshold at any temperature above 0°K. The absolute zero threshold can however be determined from measurements at ordinary temperatures. The "temperature variation of the threshold" therefore loses quantitative significance, as do recent attempts to relate this quantity to the thermionic coefficient A. Another method of testing Fowler's equation is proposed which allows the absolute zero threshold to be determined from temperature measurements at a *single frequency*, making it unnecessary to measure the relative intensities of spectral lines. The method is to plot the observations in the form $\log(I/T^2)$ vs $\log(1/T)$. The horizontal shift required to make the observed curve fit Fowler's theoretical curve ($\phi(\mu)$ vs $\log \mu$) is equal to $\log [h(\nu - \nu_0)/k]$, from which ν_0 is determined. Analysis of data for clean palladium (DuBridge and Roehr) and gold (Morris) shows a complete agreement with the theory.

43. New method for the study of the photoelectric effect of alkali vapours. JAKOB KUNZ, *University of Illinois.*—Several methods have been applied so far in the study of the photoelectric effect of alkali vapors, and yet the problem is not completely solved. The oldest method,

which I have used together with Dr. Williams is a direct one and consists in sending a beam of light through a tube with quartz windows at a given temperature. Scattering of light, photoelectric effect of a thin film of alkali deposited on the electrodes and especially the thermionic effect of such films have to be eliminated. The new method consists in using an interrupted beam of light. The photoelectric current produced plus the thermionic current pass through a condenser to an amplifying tube, in which only the photoelectric current will be amplified, while the non-interrupted thermionic current is eliminated. The system can be calibrated by means of an ordinary photoelectric cell. The second method is used for the absorption of light in alkali vapors. A monochromatic beam of ultraviolet light passes through a tube containing alkali vapor at a given temperature and falls on a photoelectric cell. The photoelectric current is measured either directly or after amplification. Another beam of light of the same source falls on a second photoelectric cell placed in series with the first cell; this method is exceedingly sensitive to small variations of light. The arrangement can also be used as null method by proper adjustment of the potentials.

44. Eotvos torsion balance. DONALD C. BARTON, *Consulting Geologist and Geophysicist, President of the Society of Petroleum, Geophysicists, Houston Texas.*—The presence of an extra heavy (or light) body in the subsurface warps the level surfaces up (down) over the body and the lines of the vertical toward or into (away from) itself. The Eotvos torsion balance consists of a calibrated platinum-iridium torsion wire which supports a beam of negligible weight; a weight is attached to one end of the beam and a second weight is suspended from the other end. Curvature of the level surfaces and curvature of the vertical each produce at the two weights horizontal components of gravity which are respectively equal and opposite in actual but the same in rotational direction. The torque produced by the curvature of the vertical is a function of the difference of the radii of curvature of the level surface in the directions of major and minor curvature. There has been only one slight important improvement of the torsion balance in the past 25 years. There is room for improvement in the avoidance of temperature effects and in speeding up in the time necessary for observation. The mathematics of the torsion balance and of the gravitational effects of simple geometrical bodies is simple and developed. The main field of research with the torsion balance lies mainly in the geological-geophysical field of interpretation, although there are still unsolved problems in the mathematics of interpretation.

45. A new instrument for measuring very small differences in gravity. KENNETH HARTLEY, *Houston, Texas.*—Description of a new portable instrument for measuring relative values of gravity to within two or three parts in ten million, specially designed for geophysical exploration. The principles of the design are analysed and the methods for eliminating effects of elastic hysteresis, temperature changes, variations in barometric pressure, etc., are discussed. Also effects of initial stresses in materials, defects in alignment of locking mechanism, inaccurate leveling, etc. These difficulties are serious but seem to have been overcome. Results of field measurements near Houston, Texas, are given and some comparison with torsion balance surveys and with known facts of structure.

46. Charts for torsion balance readings. M. M. SLOTNICK, *Humble Oil and Refining Co., Houston, Texas.*—The fact that the equations for the gradient and curvature values are linear in the differences of the readings obtained from the torsion balance makes it possible to produce easily a series of charts from which these values may be read directly, without the necessity of resorting to the slide rule or to logarithmic calculations. Two charts for each instrument, since each instrument involves different constants. One chart yields U_{zz} and U_{Δ}, and the other U_{yz} and U_{xy}. A few of these charts made for 120°-azimuth settings for Suess and Bamberg instruments will be exhibited.

47. The calculation of the motion of the ground from seismograph records. H. A. WILSON, *The Rice Institute.*—If x denotes the ground displacement and y the deflection of a mechanical seismograph then $-\ddot{x}=\ddot{y}+k\dot{y}+p^2y$. This gives $x=-y-k\int_0^t y\,dt-p^2\int_0^t\int_0^t y\,dt\,dt$. The ground displacement can therefore be found if the two integrals are evaluated graphically

or otherwise. The ground motion for a given seismogram depends very greatly upon the period and damping of the seismograph. Large errors in the calculated values of x are difficult to avoid and ground oscillations of much longer period than that of the seismograph may be entirely missed. Results obtained in this way are described. The ground motion due to a distant explosion appears to consist of several similar rapidly damped oscillations which come in at different times. An integraph is described by means of which curves, giving the above integrals as functions of t, can be quickly drawn.

48. Earth-amplitudes in seismic prospecting. MAURICE EWING, *Lehigh University.*—I. A relation between the time-distance curve and the earth amplitude-distance curve is derived upon the basis of the ray equations of geometrical optics. The possibility of using this relation in seismic prospecting is pointed out. II. The earth amplitude-distance curve is computed for several hypothetical subsurface structures consisting of two layers in each of which the velocity of propagation of seismic waves is a linear function of the depth.

49. Asymmetry of sound velocity in stratified geologic formations. BURTON MCCOLLUM AND F. A. SNELL, *McCollum Exploration Co., Houston, Texas.*—In the course of explorations of subsurface geology by the seismograph the authors have frequently observed the pronounced effect of stratification on the velocity of seismic waves in shales, and this effect has often been utilized in practical seismography. Recently an opportunity was afforded for securing additional quantitative data on the velocity normal to and parallel to the bedding planes. The paper points out that the velocity parallel to the planes of stratification is, in some instances, as much as fifty percent higher than the velocity in a direction normal to the bedding planes. It is also shown that inclined stratified beds exhibit a higher apparent point-to-point velocity when sound travels in an up dip direction than when traveling down dip. The paper describes a procedure whereby this effect may be utilized for determining the direction and approximate magnitude of the dip in such stratified deposits. The method has proved to be of considerable practical importance where the stratified formations are obscured by overlying deposits.

50. Velocity of elastic waves in granite. L. DON LEET AND W MAURICE EWING, *Harvard University and Lehigh University.*—The velocity of elastic waves in granite was determined at Quincy and Rockport, Massachusetts, and Westerly, Rhode Island. The waves measured were generated by dynamite explosions. They were recorded by portable seismographs at distances ranging from fifty feet to four thousand six hundred feet. The observed velocities for longitudinal waves were:

Quincy	$16{,}260 \pm 70$ ft/sec. or 4.96 ± 0.02 km/sec. (*)
Westerly	$16{,}400 \pm 120$ ft/sec. or 5.00 ± 0.04 km/sec.
Rockport	$16{,}670 \pm 40$ ft/sec. or 5.08 ± 0.01 km/sec.
Average	*$16{,}530 \pm 90$ ft/sec. or 5.04 ± 0.03 km/sec.*

A three-component seismograph used only at Quincy recorded transverse waves, the velocity of which was 8150 ± 90 ft/sec. or 2.48 ± 0.03 km/sec. From the two velocities determined at Quincy, and the density of specimens taken from the shooting location, 2.65 grams/cm^3, values for the bulk modulus, k, compressibility, β, rigidity, μ, Young's Modulus, E, and Poisson's Ratio, σ, were obtained as follows:

$k = 44 \pm 1 \times 10^{10}$ dynes/cm^2
$\beta = 2.28 \pm 0.05 \times 10^{-12}$ cm^2/dynes
$\mu = 16.3 \pm 0.4 \times 10^{10}$ dynes/cm^2
$E = 43 \pm 1 \times 10^{10}$ dynes/cm^2
$\sigma = 0.333 \pm 0.005$

The form of the time-distance curves, straight lines through the origin, indicated that the waves did not penetrate deeply. Accordingly, the values obtained are for pressures of at most only a few atmospheres. The bearing of these results upon earlier investigations of the elastic constants of granite is discussed. The validity of the Adams and Williamson curve for granite at pressures below 2,000 megabars is questioned, and it is concluded that there is no marked difference between dynamically and statically determined compressibilities of granite.

* The $\pm$ values given in this paper are probable errors.

51. The reflection seismograph—An application. EUGENE MCDERMOTT, *Geophysical Service, Dallas, Texas.*—The general method of operation is outlined with some reference to the earlier refraction methods. The method of determining velocity and measuring time, and the importance of correcting for the surface weathered zone are discussed. An application of the method to a faulted area in East Texas is presented with reflection records, cross sections and contour maps on two well known geological horizons.

52. Refraction profiles as aids to the reflection method. H. RUTHERFORD, *Geophysical Exploration Co., Washington, D. C.*—The relationship between the time-distance curve for refracted waves and that for reflected waves is discussed. It is shown that a refraction profile is of great assistance in identifying reflections on the records and also in determining which horizon is producing the reflections. Reflection records and time-distance graphs are shown to illustrate these points.

53. Seismological discovery and partial detail of the Vermillion Bay Salt Dome. E. E. ROSAIRE AND O. C. LESTER, JR. *Geophysical Research Corporation, Houston, Texas*—This dome is of interest because it was one of the first discovered by a seismological exploration conducted entirely by boats and over water. The organization, equipment and operation of such a crew are described. The field data resulting from this exploration are presented in full, with illustrations of the records obtained. The original interpretation of the data and the agreement with results of well drilling are presented, with criticisms in the light of later experience.

54. Some special cases of the reflection and refraction of seismic waves between similar rocks, with application to the study of crustal layers by distant quakes. LOUIS B. SLICHTER, *Massachusetts Institute of Technology*, and V. GABRILOVITCH GABRIEL, *Pasadena, Calif.*—In the first part of this paper, some particular cases of the reflection and refraction of plane elastic waves at the interface between similar rocks are computed, after the method of C. G. Knott. In the second part, the results of these computations are utilized in examining the possibility of study of a layered upper crust by means of distant, rather than local, earthquakes. For a layered crust of a type often assumed, it results that the transformed SV wave, $SP^*\overline{P}$ should produce surface amplitudes about 35 percent as large as those due to the direct wave, $SS^*\overline{S}$, when the epicentral distance is about 30°. The time lead of the derived wave $SP^*\overline{P}$ over $SS^*\overline{S}$ is here about seven seconds. The identification of this wave appears to offer difficulties, but should its recognition prove to be practicable, the study of crustal structure in regions which do not enjoy an abundance of local shocks will obviously be facilitated.

55. On the correlation of isogeothermal surfaces with the rock strata. C. E. VAN ORSTRAND, *U. S. Geological Survey.* (Published by permission of the Acting Director of the U. S Geological Survey.)—An instance of regional variation in Oklahoma, and two cases of local variation, one at Long Beach, California, and the other at Salt Creek, Wyoming, were selected for consideration from a rather large number of geothermal surveys conducted during the past few years by the U. S. Geological Survey and the American Petroleum Institute. As no theory has been developed to explain either the local or regional variations, it is not claimed that the results of the surveys, or the conclusions reached in regard to them, are necessarily applicable to other fields. Radioactivity, proximity to crystalline rocks, and transfer of heat along the strata are given careful consideration in attempting to explain the observed relations between the strata and the isogeothermal surfaces.

56. Geothermal gradient determinations in the Lake Superior copper mines. L. R. INGERSOLL, *University of Wisconsin.*—The Michigan College of Mining and Technology, in cooperation with the Calumet and Hecla Copper Company and the author, is carrying out a program of temperature measurements in the deep copper mines of Northern Michigan, extending the previous work of Agassiz and others. Temperatures are measured with mercury thermometers mounted in Bakelite tubes, placed in drill holes in mine workings where the rock has been freshly exposed, special attention being given the effects of drilling, blasting, and other heat conduction considerations. Present results give as the average gradient from the surface

to 5679 feet below (temp. 95.3°F), 1°F in 108.5 feet (0.0168°C/meter). The gradient is more nearly uniform than has sometimes been supposed. A preliminary attempt has been made at calculating the previous "thermal history" of this region. Diffusivity of specimens of the rock measures 0.0075 c.g.s. (for method see Ingersoll and Koepp, Phys. Rev. **24,** 92, 1924) and on this basis calculations of theoretical temperature-depth curves have been made for 25 different assumptions of previous temperature conditions, and compared with the actual curve. Results as yet are inconclusive but indicate that at least 30,000 years have elapsed since the last glacial epoch, a longer period than usually assumed.

57. Electrical prospecting as applied in locating oil structures. LEO J. PETERS AND JOHN BARDEEN, *Gulf Research Laboratory, Pittsburgh.*—This paper discussed in a general way the basic ideas upon which electrical prospecting is based. It gives a few of the more successful ways of carrying out these basic ideas and presents some surveys which show the extent to which success in mapping oil structures has been obtained.

58. The luminescence of solid nitrogen. JOSEPH KAPLAN, *University of California at Los Angeles.*—An explanation is proposed for all of the radiations that have been observed by Mc Lennan and his collaborators in the luminescence of solid nitrogen. The bands are associated with known bands of the second, fourth and first positive groups of nitrogen; with hitherto unobserved second-positive bands; with a new intercombination system and with new modifications of the first-positive bands. These new modifications of the first-positive bands are related to the spectra of the aurora, night-sky and planetary absorption spectra. As a result of this correlation, it is now possible to see why Vegard identified the aurora spectrum as the spectrum of solid nitrogen and then proposed his theory of the upper atmosphere.

59. Dirac's equation and the spin-spin interaction of two electrons. G. BREIT, *New York University.*—In a previous paper (Phys. Rev. **34,** p. 553) an equation has been set up for the treatment of two electrons. This equation is

$$\left\{ p_0 + \mathbf{a}^{\mathrm{I}}\mathbf{p}^{\mathrm{I}} + \mathbf{a}^{\mathrm{II}}\mathbf{p}^{\mathrm{II}} + (\alpha_4^{\mathrm{II}} + \alpha_4^{\mathrm{I}})mc + \frac{e^2}{2c}\left(\frac{\mathbf{a}^{\mathrm{I}}\mathbf{a}^{\mathrm{II}}}{r_{\mathrm{I\,II}}} + \frac{(\mathbf{a}^{\mathrm{I}}\mathbf{r})(\mathbf{a}^{\mathrm{II}}\mathbf{r})}{r_{\mathrm{I\,II}}^3} \right) \right\} \psi = 0.$$

The notation is that of Dirac, and Roman numerals refer to the two electrons. The wave function ψ has 16 components. At the time the difficulty of negative energies made it plausible to regard the above equation as being correct only inasmuch as it determines relations between the four largest components, ψ_{23}, ψ_{44}, ψ_{34}, ψ_{43}. In the applications (Phys. Rev. **36,** p. 385) the integrability of $\sum_{\alpha,\beta=3,4}\psi_{\alpha\beta}^*\psi_{\alpha\beta}$ and the equations for $\psi_{\alpha\beta}$ were therefore used. These equations had to be modified in order to bring about agreement with the fine structure of He. It is now shown that if the integrability of $\sum_{\mu,\nu=1,2,3,4}\psi_{\mu\nu}^*\psi_{\mu\nu}$ is required and all of the 16 components of ψ are used the previously troublesome terms in e^4 disappear automatically. With this restricting condition the above equation is thus in agreement with the observed spin-spin interactions in He^{I} and Li^{II}.

60. The far infrared transmissions of various solids. R. BOWLING BARNES, *Physikalisches Institut, Berlin.*—Using a wire grating spectrometer transmission curves have been measured for 12 substances from 20μ to 135μ. In fused quartz absorption bands have been found at 39μ, 86μ, 118μ and $\lambda > 132\mu$. In crystalline quartz, at 26μ, 38μ, 77μ, 105μ and 122μ. In sulphur bands occur at 21, 5μ, 25, 0μ, 37, 5μ, 40μ to 50μ, 67μ, 96 μ, 114, 5μ and $\lambda > 130\mu$. In paraffin, 82, 5μ, 106μ, and 127, 5μ. In mica 5μ thick, bands are found at 27μ, 33μ, 60μ, 95μ and at 123μ. A discussion of these absorptions including the curves for these 5 substances and the other 7 will appear at an early date.

61. The thin plate. D. G. BOURGIN, *University of Illinois.*—The problem of the very thin plate, for large displacements when bending stresses may be neglected, has been treated by Hencky by a numerical approximation method. His results for the rectangular plate are incorrect because of invalid boundary conditions. This paper derives a solution by the hitherto

unused method in elasticity problems of working directly with the stresses rather than the displacements. Experimental results of A. Falk on the bending of a steel sheet 10 in. $\times$10 in. $\times$0.05 in. are in accord with the assumption of negligible bending stress for this case.

62. Experimental establishment of the relativity of time. Roy J. Kennedy and Edward M. Thorndike, *California Institute of Technology.*—None of the fundamental experiments on which the restricted principle of relativity is based requires for its explanation that the classical concept of absolute time be modified; the present experiment was devised to test directly whether time satisfies the requirements of relativity. It depends on the fact that if a pencil of homogeneous light is split into two components which are made to interfere after traversing paths of different length, their relative phases will depend on the translational velocity of the optical system unless the Lorentz-Einstein transformation equations are valid. Hence such a system at a point on the earth should give rise to an interference pattern which varies periodically as the velocity of the point changes in consequence of the rotation and revolution of the earth. The effect to be expected for a small velocity is so very small that it has been necessary to devise a special source of light, an interferometer of great stability and a refinement of the technic of measuring displacements in the interference pattern. With the apparatus finally employed, we have shown that there is no effect corresponding to absolute time unless the velocity of the solar system in space is no more than about half that of the earth in its orbit. Using this null result and that of the Michelson-Morley experiment we derive the Lorentz-Einstein transformations, which are tantamount to the relativity principle.

63. On the law of force between the molecules in a liquid or gaseous mixture. R. D. Kleeman, *Schenectady, New York.* (*Introduced by W. L. Severinghaus.*)—The author has previously deduced from various data the nature of the law of force between two molecules in a pure liquid or gas. It was found that this force is given by $\phi[(T/T_c), (Z/x_c)]\cdot(\Sigma c_a)^2/Z^5$, where Z denotes the distance of separation of the molecules at the absolute temperature T, x_c the average minimum distance of separation of the molecules at the critical temperature T_c, Σc_a the sum of a number of constants each of which refers to an atom of a molecule, and ϕ a function of the quantities x_c, Z, T, T_c, which may be determined from the equation of state of the substance. The constant c_a is approximately proportional to the two thirds power of the atomic number of the atom.* It is now shown that in the case of a mixture of two substances the law of force is $K(\Sigma c_a)(\Sigma c_e)/Z^5$ where Σc_a refers to one of the substances and Σc_e to the other, and K is a quantity varying little with T.

64. The "flash" in the afterglow of argon with a fixed vacuum. Chas. T. Knipp, *University of Illinois.*—In a recent number of the Philosophical Magazine the writer and L. E. Scheuerman described a "flash" that appeared in the afterglow of certain gases, notably nitrogen, when the residual gas *was suddenly compressed.* Just recently (December 4th, to be exact) the writer while exhibiting the electrodeless discharge in a liter pyrex flash at the Butler meeting of the Indiana Academy of Science observed a flash in the afterglow with a *fixed* vacuum. This particular tube contains argon at a pressure of between 0.1 and 0.2 mm of mercury, and was prepared last May. No record was kept of the moisture present, or of the purity of the gas. Mr. H. C. Roberts, Assistant to the writer, said that this peculiar action of the gas was observed and briefly commented upon at the time that the tube was sealed off, but for some reason the phenomenon was passed by until the striking observation was again made as referred to above. No definite experimental theory has as yet been attempted nor has there been time to make even the most elementary observations, spectroscopically or otherwise, of this apparent recalescent phenomenon in a gas. The flash in this bulb occurs within two or three seconds after the energizing source has been removed and is of sufficient brightness to be observed by reflection on a nearby screen. Following this the intensity of the afterglow changes color slightly and dies off rapidly. It would be interesting to note whether additional flashes occur on the decay curve, possibly flashes that the eye could not detect.

* A book on the subject is "The Atomic and Molecular Forces of Chemical and Physical Interaction in Liquids and Gases, and their Effects" by R. D. Kleeman B.A., D.Sc. (Taylor and Francis, Red Lion Court, Fleet Street, London, England).

AUTHOR INDEX TO ABSTRACTS OF THE NEW ORLEANS MEETING

Banta, H. E.—No. 23
Bardeen, John—see Peters
Barnes, R. Bowling—No. 60
Barton, Donald C.—No. 44
Beams, J. W.—No. 9
Bearden, J. A.—No. 19
Boner, C. P. and Marion O. Boner—No. 28
Boner, Marion O.—see Boner
Bonner, T. W.—No. 14
Bourgin, D. G.—No. 61
Bowie, R. M.—see Carr
Breit, G.—No. 59
Brickwedde, F. G.—see Urey
Brown, S. Leroy—No. 29
Bryan, A. B.—see Zirbel

Cady, W. G.—No. 24
Carlson, J. F. and J. R. Oppenheimer—No. 35
Carr, P. H. and R. M. Bowie—No. 10
Chambers, Leslie A.—see Gaines
Colby, M. Y.—No. 21

Decherd, Loraine and Arnold Romberg—No. 7
DuBridge, L. A.—No. 42
——— see Roehr

Ewing, Maurice—No. 48
——— see Leet

Gabriel, V. Gabrilovitch—see Slichter
Gaines, Newton and Leslie A. Chambers—No. 25
Germond, H. H.—No. 11
Gunn, Ross—No. 6

Hardy, J. D.—see Van Lear
Hartley, Kenneth—No. 45
Hidnert, Peter—No. 1
Hughes, A. L. and J. H. McMillen—No. 37
——— see McMillen
Hutchisson, Elmer—see Muskat

Ingersoll, L. R.—No. 56

Kaplan, Joseph—Nos. 18, 58
Karrer, E.—No. 4
Kennedy, Roy J. and Edward M. Thorndike—No. 62
Kleeman, R. D.—No. 63
Knipp, Chas. T.—No. 64
Kunz, Jakob—No. 43
Kurie, F. N. D.—No. 36

LaCoste, Lucien—No. 20
Lawrence, Ernest O. and M. Stanley Livingston—No. 26
Leet, L. Don and W. Maurice Ewing—No. 50
Lester, O. C., Jr.—see Rosaire
Livingston, M. Stanley—see Lawrence
Locher, Gordon L.—No. 40

MacColl, L. A.—No. 12
Margenau, Henry—No. 17
McCollum, Burton and F. A. Snell—No. 49
McDermott, Eugene—No. 51
McMillen, J. H. and A. L. Hughes—No. 38
——— see Hughes
Mooney, R. C. L.—No. 22
Murphy, G. M.—see Urey
Muskat, Morris and Elmer Hutchisson—No. 13

Oppenheimer, J. R.—see Carlson

Penney, W. G.—No. 15
Peters, Leo J. and John Bardeen—No. 57
Pietenpol, W. B. and G. W. Presnell—No. 27
Presnell, G. W.—see Pietenpol

Rabi, I. I.—No. 33
Ransome, W. R.—No. 8
Roehr, W. W. and L. A. DuBridge—No. 41
Roller, Duane and Hughes Zenor—No. 39
Romberg, Arnold—see Decherd
Rosaire, E. E. and O. C. Lester, Jr.—No. 53
Rupp, E. and L. Szilard—No. 32
Rutherford, H.—No. 52

Slichter, Louis B. and V. Gabrilovitch Gabriel—No. 54
Slotnick, M. M.—No. 46
Snell, F. A.—see McCollum
Szilard, L.—see Rupp

Thorndike, Edward M.—see Kennedy
Tykociner, J. Tykocinski—No. 31

Urey, Harold C., F. G. Brickwedde, and G. M. Murphy—No. 34

Van Lear, G. A., Jr. and J. D. Hardy—No. 3
Van Orstrand, C. E.—No. 55

Whitford, Albert E.—No. 16
Wilson, H. A.—No. 47
Woods, J. P.—No. 30

Zeleny, Anthony—No. 5
Zenor, Hughes—see Roller
Zirbel, N. N. and A. B. Bryan—No. 2

CURRENT LITERATURE OF PHYSICS

Extracts from the Tables of Contents of Some of our Contemporaries

PHILOSOPHICAL MAGAZINE

SERIES 7, VOL. 13, No. 83 FEBRUARY, 1932

Hall Effect and Other Physical Properties of the Copper-Cadmium Series of Alloys. By **Wallace Richards and E. J. Evans** 201
Kinetics of a Catalysed Isomeric Change in Solution. By **R. C. Traill** 225
Magneto-Resistance and Magneto-Caloric Effects in Iron and Heusler Alloys. By **H. H. Potter** 233
On the Variations in the Refractive Index of Benzene during Intensive Drying. By **J. J. Manley** 249
Magneto-Optical Dispersion of Organic Liquids in the Ultraviolet Region of the Spectrum.—Part IV. The Magneto-Optical Dispersion of Acetic Anhydride, Normal Butyric Acid, and Normal Ethyl Butyrate. By **W. J. Lewis and E. J. Evans** 265
Activities and the Standard State.—I. Activity Coefficients. By **Angus MacFarlane and Oliver Gatty** 283
Activities and the Standard State.—II. Electrode Potentials. By **Oliver Gatty and Angus MacFarlane** 291
Application of Piezo-electricity to Microscopy. By E. H. Synge 297
Attempt to Detect High Photoelectric Absorption in Caesium Vapour at Double the Series Limit. By **E. T. S. Appleyard** 300
On the Raman Effect from the Standpoint of Unimolecular Reactions By **A. Ganguli** 306
The More Accurate Calculation of the Deflexion of Beams and Struts. By **H. H. Jeffcott** .. 310

PHILOSOPHICAL MAGAZINE

Supplementary Number

SERIES 7, VOL. 13, No. 84 FEBRUARY, 1932

nhv Emission in Xenon and Thallium iii By **W. M. Hicks** 329
Lattice Distortion and Hardness of Heat-treated Tungsten Magnet Steels. By **W. A. Wood** 355
Note on the Transport Phenomena in a Degenerate Gas.—Part I. By **D. S. Kothari** 361
Determination of the Stefan-Boltzmann Radiation Constant, using a Callendar Radio Balance. By **F. E. Hoare** 380
Thermoelectric Properties of Ferromagnetic Substances. By **L. F. Bates** 393
X-ray Examination of Iron-Chromium Alloys. By **G. D. Preston** 419
Standard Electrode Potentials in Ethyl Alcohol. By **Angus MacFarlane and Sir Harold Hartley** 425
Effect of Electrolytes on the Dielectric Constant of Water.—Parts III. and IV. By **R. T. Lattey and W. G. Davies** 444
Raman Spectra in Liquid and Gaseous CH_4. By **Susil Chandra Biswas** 455
Stabilizing Effect of Imposed Oscillations of High Frequency on a Dynamical System. By **E. R. Lowenstern** 458
Light Intensities of Neon Discharges. By **P. Johnson** 487
On the Distribution of Space-potential in Striated and Other Forms of High-frequency Discharge. By **D. Banerji and R. Ganguli** 494
Search for the Band Spectra of Boron Fluoride. By **N. R. Tawde and R. C. Johnson** 501
On the Absorption of X-rays in Gases and Vapours.—Part II. By **J. A. Crowther** 505
Theory of Coagulation of Homogeneous Aerosols. By **H. S. Patterson** 523

NATURE

Vol. 129, No. 3247 — January 23, 1932

Metallic State. By **Allan Ferguson** ... 116

Letters to the Editor:

Raman Lines and Infrared Bands in Nitrous Oxide. By **E. F. Barker** ... 132

Selective Action of Living Tissue to Homogeneous Radiation. By **W. Moppett** ... 133

Effect of Light on the Surface Tension of Boys's Soap Solution. By **L. D. Mahajan** ... 133

NATURE

Vol. 129, No. 3249 — February 6, 1932

Letters to the Editor:

Specific Heats of the Diatomic Gases. By **P. S. H. Henry** ... 200

Surface Convection and the Distribution of Temperature near a Heated Surface. By **L. A. Ramdas and S. L. Malurkar** ... 201

Gill-Morell and Barkhausen-Kurz Oscillations. By **R. Cockburn** ... 202

Air Column Resonances and Symmetrical Modes of Truncated Conical Shells (Loud Speaker Diaphragms). By **N. W. McLachlan** ... 202

Propagation of Hertzian Waves in Electronic Gas under the Influence of a Magnetic Field. By **G. Todesco** ... 203

Method of High-Frequency Stroboscopy. By **J. A. Strong** ... 203

Hyperfine Structure of the Mercury Line λ 4916. By **S. Tolansky** ... 204

Photoreduction of Carbonic Acid, Bicarbonates, and Carbonates to Formaldehyde. By **N. R. Dhar and Atma Ram** ... 205

Helmholtz or Kelvin Cloud Waves. By **Sir Gilbert Walker** ... 205

ZEITSCHRIFT FÜR PHYSIK

Vol. 73, Nos. 11 and 12 — January 15, 1932

Spectral Photoelectric Sensitivity of Thin Alkali Metal Films at Room Temperature and at the Temperature of Liquid Air. By **S. Suhrmann and H. Theissing** ... 709

On the Transition from Glow to Arc Discharge in the Noble Gases. By **M. J. Druyvesteyn** 727

Band Spectrum of Beryllium Hydride. By **Ernst Olsson** ... 732

Negative Nitrogen Bands. By **D. Coster and H. H. Brons** ... 747

On the Question of the Mechanism of Electrical Breakdown. By **A. Joffé, P. Kobeko, J. Kurtschatov and Anton Walther** ... 775

On the Tensile Strength of Thin Filaments and Foils. By **A. Joffé, S. Schurkov and Anton Walther** ... 778

On the Spectram of the Noble Gases. By **Ebbe Rasmussen** ... 779

Interpretation of the Infrared Spectrum of Polytomic Molecules. By **E. Teller and L. Tisza** 791

On the Velocity of Propogation of Supersonic Oscillations in Cylindrical Rods. By **Karl Rohrich** ... 813

On a New Method for the Testing of the Law of Brownian Movement. By **E. M. Brumberg and S. I. Wawilow** ... 833

ZEITSCHRIFT FÜR PHYSIK

Series 1 and 2, Vol. 74 — January 22, 1932

On the Theory of High Melting Non-Conducting Atomic Lattices. By **F. Hund** ... 1

Quenching of Resonance Band Spectra and Energy Transfer by Admixed Gases. By **Oskar Heil** ... 18

Remark on an Article of Kneser on the Velocity of Sound in CO_2. By **Oskar Heil** ... 31

On the Absorption Spectrum of IBr in the Visible. By **H. Cordes** ... 34

Plasticity and Rigidity of Notched Rods. By **W. Kuntze** ... 45

On the Determination of the Pressure in Explosion Waves in Air. By **W. Schneider** ... 66

On Second Order Laws in Simple Symmetric Systems. By **M. Herzberger.** ... 88

On Two Different States of a Liquid. By **M. Wolkfe and J. Mazur** ... 110

On the Demonstration of Different Ferromagnetic States of Solid Bodies. By **W. Gerlach** 128

Dynamics of Free Rectangular Plates. By **Harry Schmidt** ... 130

Note on the Relation Between Dynamical and Statistical Laws. By **Hermann von Schelling** ... 140

DIE NATURWISSENSCHAFTEN

SERIES 4, VOL. 20 — JANUARY 22, 1932

Address on the Seventieth Birthday of David Hilbert. By **H. Weyl** 57

Short Original Contributions

Experimental Test of the Theory of Weisskopf and Wigners on Natural Line Width. By **Wilhelm Schütz** 64

Measurements of the Absorption of Penetrating Corpuscular Rays in One Meter of Lead. By **Bruno Rossi** 65

DIE NATURWISSENSCHAFTEN

SERIES 5, VOL. 20 — JANUARY 29, 1932

Short Original Contributions

Regularities Between α and β Radioactive Decay Constants. By **J. Kudar** 84

Red Oxygen Radiation of the Night Heaven. By **W. Grotrian** 85

On the Nuclear Moment of Se_{80}. By **K. Wurm** 85

On the Time Necessary for the Attainment of Thermal Equilibrium of Vibrational Energy of Diatomic Molecules. By **A. Eucken, O. Mücke and R. Becker** 85

On the Lead and Helium Content of Oceanic Alkali Halides. By **Otto Hahn** 86

On the Time Lag of Spark Discharge. By **Fritz Bath and W. Kaufmann** 87

PHYSIKALISCHE ZEITSCHRIFT

VOL. 33, NO. 3 — FEBRUARY 1, 1932

Review of the Subject of Atomic Factors. By **W. Ehrenberg and K. Schaefer** 97

Original Communications:

Scattering of X-rays in Simple Gases (N_2, O_2, CO_2, CS_2, NH_3, H_2O). By **H. Gajewski** 122

On the Capacities of Electrometers. By **L. Dees** 131

On the Methods of Determining the Constants and the Capacity of Quadrant Electrometers. By **G. Nadjakoff** 135

The Quantitative Law for the Viscosity of Simple Strong Electrolytes. By **H. Falkenhagen and E. L. Vernon** 140

COMPTES RENDUS

VOL. 194, NO. 4 — JANUARY 25, 1932

On the High Frequency Discharge. By **C. Gutton and G. Beauvais** 338

Letters

Equilibrium Potentials of an Insulated Electrode of a Triode. By **G. A. Beauvais** 358

Production of Positive Ions of High Velocity by Multiple Acceleration. By **Jean Thibaud** 360

Powerful Spectrograph for Diverging X-rays Reflected from a Bent Mica Sheet. By **Y. Cauchois** 362

Astigmatism of a Pencil of Rays Obliquely Refracted by a Spherical Diopter. By **Marcel Dufour** 365

Rotation of Naphthalene Bis-imino-camphor and the Theory of Werner Kuhn. By **J. P. Mathieu** 367

Rotatory Dispersion in the Ultraviolet of α and β pinenes in Solutions in Ethyl Alcohol. By **Roger Servant** 368

Ionization Chambers of Very Small Dimensions for the Localized Measurement of Gamma Rays. By **Lucien Mallet** 370

LE JOURNAL DE PHYSIQUE

SERIES VII, VOL. III, NO. 1 — JANUARY, 1932

On the Birefringence Due to Compression of Amorphous Silica and of Crystalline Quartz and its Dispersion in the Ultraviolet. By **G. Bruhat and J. Thouvenin** 1

On the Distribution of Ozone in the Terrestrial Atmosphere. By **D. Chalonge** 21

Ultraviolet Absorption of Optically Active Mixed Organic Solutions. By **R. Lucas and M. Schwob** 43

PHYSICS

No. 2 — JANUARY 12, 1932

Investigations of the Oscillatory Condensor Discharge. By **U. Ph. Lely**. 33
Kinetic Derivation of the Law of Van't Hoff for the Osmotic Pressure of Dilute Solutions. By **J. W. Dekker**. 38
On the Moment of Inertia in Torsional Oscillations. By **H. J. Oosting**. 56
Electromagnetic Apparatus for the Generation of Torsional Oscillations. By **H. J. Oosting**. 60

JOURNAL OF RHEOLOGY

VOL. 3, No. 1 — JANUARY, 1932

The Cause of Fluctuations in Rising Mixtures of Gas and Liquid. By **J. Versluys**. 3
Fundamental Equations and Definitions concerning the Mechanics of Isotropic Continua. By **K. Hohenemser and W. Prager**. 16
Dimensional Analysis of Plastic Flow. By **Mayo D. Hersey**. 23
On a Simple Model Explaining the Hardening Effect of Poly-Crystalline Metals. By **H. Hencky**. 30
The Influence of Nitrogen in Mild Steel on the Ability of Developing Flow Layers. By **C. W. MacGregor and F. R. Hensel**. 37
Some Physical Properties of Wiping Solders. By **D. A. McLean, R. L. Peek, Jr., and E. E. Schumacher**. 53
Thixotropy and Plasticity. I—The Measurement of Thixotropy. By **Elliott L. McMillen**. 75
The Mixture Law. By **Eugene C. Bingham and Delbert F. Brown**. 95
The Fluidities of Non-Aqueous Mixtures. By **Eugene C. Bingham and Horace E. Rogers**. 113
Viscosity Measurements in Molten Glass. By **Howard R. Lillie**. 121

PHYSICS

VOL. 2, No. 2 — FEBRUARY, 1932

Precision Method of Measuring Small Changes of Lattice Spacings of Metal Single Crystals. By **Rudolf C. Hergenrother**. 63
Attempt to Activate Adsorbed Mercury Atoms by Ultraviolet Light. By **L. H. Reyerson**. 70
Potential Distribution, Radiation and Electrical Conduction in Paper. By **Edward B. Baker and Robert F. James**. 73
Dielectric Loss and Relaxation Time in Rosin. By **J. B. Whitehead**. 82
Heat Waves Through Insulating Walls. By **Emerson M. Pugh and F. C. Houghten**. 93